JIHOČESKÁ UNIVERSITA

Přírodovědecká fakulta

RNDr. Dana Nachtigallová, PhD.

CHARACTERIZATION OF CHROMOPHORES IN ELECTRONICALLY EXCITED STATES BY MEANS OF COMPUTATIONAL METHODS

CHARAKTERIZACE CHROMOFÓRŮ V ELEKTRONICKY EXCITOVANÝCH STAVECH POMOCÍ VÝPOČETNÍCH METOD

Habilitační práce

Praha, 2024

Poděkování

Děkuji všem kolegům ze skupiny Prof. Pavla Hobzy za trvalý zájem a podporu své vědecké práce, a zejména za vytvoření tvůrčího, motivačního a inspirativního prostředí.

Děkuji také svým váženým vědeckým kolegům prof. Hans Lischkovi, Prof. Mattanjah deVriesovi a prof. Petru Klánovi za intenzivní, dlouholetou a obohacující spolupráci v oboru chemie a fyziky excitovaných stavů.

Jsem si vědoma, že bez dlouholeté podpory vedení Ústavu Organické chemie a biochemie, AV ČR bych tuto práci nemohla předložit.

Prohlášení

Prohlašuji, že jsem tuto habilitační práce zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu.

V Praze, dne 22.4.2024

Obsah

1. Úvod

Habilitační práce předkládá výsledky studií, jejichž společným tématem je charakterizace excitovaných stavů. Modelování excitovaných stavů je ilustrováno na dvou typech systémů: (1) polyaromické uhlovodíky a odvozené systémy jako modely kvantových teček v základním a excitovaných stavech a (2) excitované stavy isolovaných systémů bází nukleových kyselin a jejich modifikací, a bází interagujících pomocí nekovalentních interakcí. Práce, na kterých se autorka podílela, jsou specificky zmíněny a zařazeny do kontextu tehdejších studií na dvou uvedených systémech. Jevy, na jejichž studiu se autorka nepodílela, jsou zmíněny pouze okrajově z důvodu zachování tematické celistvosti.

1.1. Charakterizace excitovaných stavů

Určení eletronové struktury molekuly v základním stavu je prvním krokem procesu její charakterizace, včetně chemických vlastností a reaktivity. Charakter elektronové struktury převážné většiny molekul v základním stavu dovoluje popis systému pomocí jedné elektronové konfigurace (jedno-referenční popis). Vhodným ukazatelem je dostatečný energetický rozdíl mezi 'highest occupied molecular orbital' (HOMO) a 'lowest unoccupied molecular orbital' (LUMO). Pro některé systémy a procesy, např. existuje-li více energeticky blízkých elektronových konfigurací (systémy s d-orbitaly ve valenční slupce, radikály), reakce molekul zahrnující tvorbu nebo přerušení chemické vazby a procesy v excitovaných stavech, je tento popis nedostatečný. Tyto systémy se nazývají multi-referenční a pro jejich popis je třeba zahrnout další elektronové konfigurace.[1]

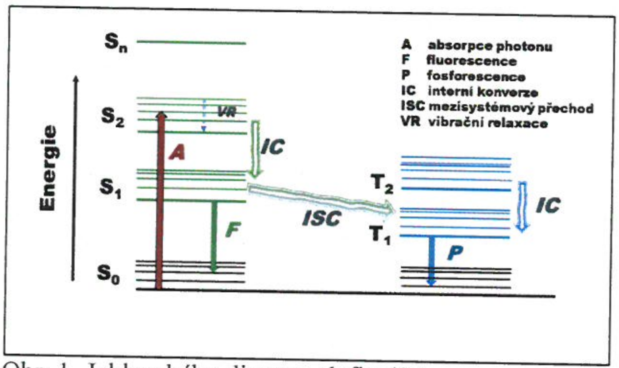
Popis procesů probíhajících v excitovaných stavech navíc zahrnuje situace, ve kterých selhává jedna ze základních aproximací kvantové chemie, Born-Oppernheimerova aproximace (BOA) separující elektronový a jaderný pohyb. Tato separace je klíčovým předpokladem řešení Schrödingerovy rovnice a spolu s Franck-Condonovým principem, který říká, že k elektronickému přechodu s největší pravděpodobností dojde beze změn polohy jader v molekule a jejím okolí, tvoří základ pro výpočet elektronických spekter.[2–4] Mimo Franck-Condonovu oblast může dojít k situaci, kdy se k sobě dva nebo více povrchů potenciální energie (PES) energeticky přiblíží, a tak se pohyby jader a elektronů propojí a BOA selhává. Tato situace otevírá témata fotoindukovaných procesů,[5] neadiabatické fotodynamiky[6] a neadiabatických interakcí.[7,8] Aparát pro popis neadiabatických procesů bude ilustrován v dalším textu.

Molekulární procesy indukované UV/VIS zářením hrají významnou roli v mnoha vědeckých a technologických oborech. Pro experimentálni i teoretické chemiky je odlišné chování molekul v elektronicky excitovaných stavech ve srovnání se základním stavem skutečnou výzvou. Experimentálni metody, jmenovitě konvenční stacionární spektroskopie[9] a její rozšíření na časově rozlišenou spektroskopii,[10] jsou schopny popsat systémy v excitovaných stavech s velkou přesností. Pro interpretaci těchto dat jsou vzhledem ke komplexnímu chování molekul v excitovaných stavech výpočetní metody nezbytným prostředkem.

1.2 Terminologie pro popis excitovaných stavů

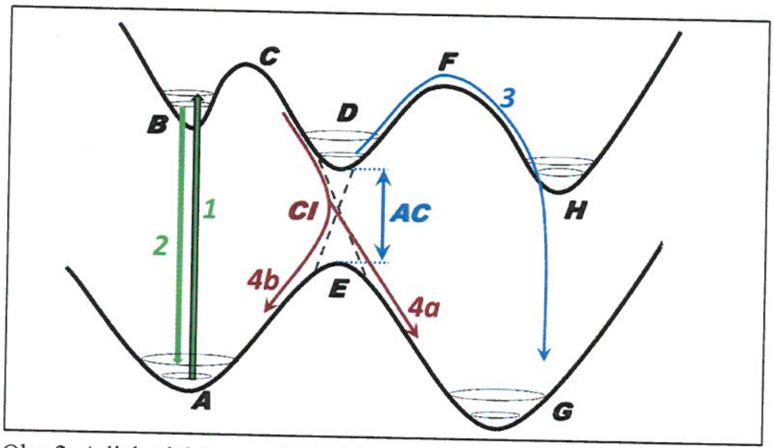
Elektronové stavy molekuly a přechody mezi nimi shrnuje Jablonského diagram (Obr. 1). Absorpce elektromagnetického záření **A** UV nebo viditelných vlnových délek vede k vybuzení molekuly do nerovnovážného stavu, z kterého se spustí sekvence relaxačních procesů.

Tyto procesy mohou odpovídat vibrační relaxaci **VR** na jedné PES, neradiačnímu přechodu na jinou adiabatickou PES stavu se stejnou (vniřní konverze, **IC**) nebo rozdílnou spinovou multiplicitou (mezisystémový přechod, **ISC**), případně radiačním přechodům, tj. fluorescenci **F** nebo fosforescenci **P**. Relaxační procesy probíhají v časovém rozpětí v řádu několika desítek femtosekund, což odpovídá vibračním relaxacím, až milisekund, odpovídající fosforescenci, tedy v časovém rozpětí více než deseti řádů.



Obr. 1. Jablonského diagram definující procesy: absorpce fotonu (A), fluorescence (F), fosforescence (P), interní konverze (IC), mezisystémový přechod (ISC), vibrační relaxace (VR)

Po absorpci světla v bodě ***A*** systém přejde do bodu ***B*** ve Franckově-Condonově oblasti (proces **1** na Obr. 2). Po nalezení minima excitovaného stavu se systém může vrátit do základního stavu emisí světla (proces **2** na Obr. 2) nebo zůstat v excitovaném stavu. V druhém případě se systém vyvíjí ve třech následujících procesech: (i) setrvává po nějakou dobu v excitovaném stavu, kde může případně interagovat s jinými excitovanými stavy (viz níže), (ii) následně relaxuje do základního stavu a (iii) sleduje PES základního stavu do minima. Jak znázorňuje Obr. 2, při dostatečně velké počáteční energii (proces **1**) systém překoná bariéru transitního stavu ***C*** a přejde k blízkosti minima excitovaného stavu, tj. do bodu ***D***, z kterého může následovat dvě možné cesty. V prvním případě se povrchy v místě pseudo-křížení základní a excitované PES (body ***D*** a ***E***) nekříží (tzv. avoided crossing, ***AC*** na Obr. 2), systém setrvá na excitované PES a přes transitní stav ***F*** přejde do dalšího minima excitovaného stavu ***H***, odkud relaxuje do základního stavu ***G***, které není identické s ***A***, tzn. vzniká tzv. fotoprodukt. Tento proces, znázorněný křivkou **3**, probíhá až do bodu ***H*** beze změny elektronického stavu a je označován za adiabatický. V druhém případě se křivky kříží v bodě zvaném kónická intersekce (conical intersection, ***CI*** na Obr. 2), relaxační proces probíhá na dvou PES a odpovídající mechanismus je neadiabatický. Jak vyplývá z obr. 2, systém může relaxovat jak do minima ***G*** za vzniku fotoproduktu (křivka **4a**), tak do původního minima ***A*** (křivka **4b**). V druhém případě mluvíme o fotostabilním systému. Na rozdíl od adiabatického mechanismu, kdy je systém v minimu ***D*** charakterizován konečnou dobou života, procesy probíhající v ***CI*** jsou mimořádně rychlé, v časovém intervalu molekulových vibrací, a systém tak není možné v tomto stavu experimentálně zachytit.



Obr. 2. Adiabatické a neadiabatické procesy na křivkách potenciální energie dvou stavů.

1.3 Excimery, exciplexy a excitony

V případě absorpce UV záření systému s větším množstvím absorbujících skupin (chromophorů) může dojít k jejich interakci v excitovaných stavech. Tyto interakce jsou výsledkem dvou hlavních příspěvků:

(1) Coulombické interakce, tzv. ´long-range´, které lze popsat interakcí transitních dipólových momentů nebo vyšších multipólů a závisí na vzdálenosti chromophorů (R) jako R^{-3}

(2) tzv. ´short-range´ interakce, které jsou výsledkem překryvu orbitalů zapojených do excitace. Dosah těchto interakcí klesá exponenciálně s R.

Podle povahy excitace lze excitované komplexy popsat v termínech lokalizovaných a ´charge-transfer´ (CT) přechodů:

$$\Psi_{exc} = c_1\psi(A^*B) + c_2\psi(AB^*) + c_3\psi(A^-B^+) + c_4\psi(A^+B^-), \tag{1}$$

kde $\psi(A^{*}B)$ a $\psi(AB^{*})$ odpovídá excitacím lokalizovaným na A nebo B a $\psi(A^{-}B^{+})$ a $\psi(A^{+}B^{-})$ popisuje CT stavy, při kterých dochází k přenosu náboje.[11] Je-li A identické s B a $c_1 = c_2$, $c_3 = c_4$, výsledný komplex se nazývá excimerem, v opačném případě se jedná o exciplex.

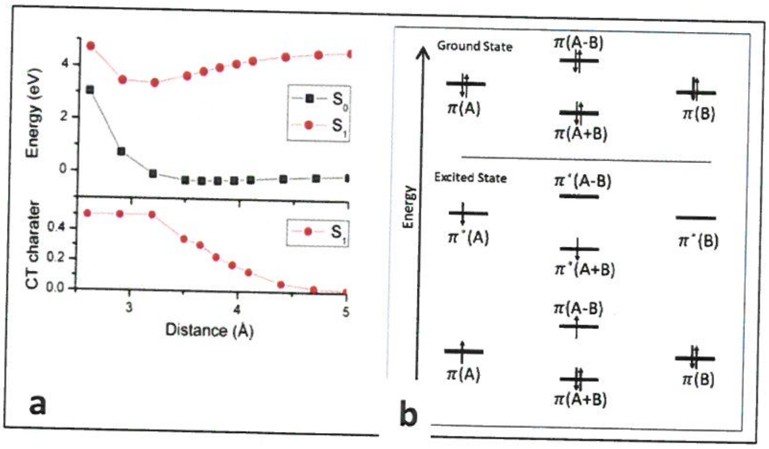
Povahu a rozsah interakce a tvorbu excimeru/exciplexu názorně ilustruje Obr. (3a) na příkladu dvou naphthalenů v symetrickém uspořádání.[11] V základním stavu tvoří dimer slabě vázaný komplex s mělkým minimem v R≅3.65 Å (získané výpočtem ADC(2) metodou) se stabilizační energií menší než 0.1 eV. V excitovaném stavu je stabilizační energie 1.32 eV s minimem v R≅3.2 Å. Povaha interakce v dimeru v excitovaném stavu je ilustrována příspěvky elektronových konfigurací s CT charakterem (Obr. 3a, spodní graf). V R>5 Å jsou CT příspěvky nevýznamné a dimer má charakter tzv Frenkelova excitonu, který lze popsat Frenkelovou excitonovou terorií, podle které je celkový Hamiltonián systému vyjádřen výrazem

$$H = \sum\nolimits_{A} H_A + \sum\nolimits_{A} \sum\nolimits_{B>A} V_{AB}, \tag{2}$$

kde H_A odpovídá isolovaným chromophorům a V_{AB} je interagující člen. Vlnovou funkci excitonu vyjadřuje tvar

$$\Psi_k = \sum\nolimits_{A} c_{kA}\, \phi_A^i, \tag{3}$$

kde ϕ_A^i je vlnová funkce excitovaného chromophoru A.



Obr. 3 a) Horní graf: Závislost stability naphthalene dimer v základním (S_0) a excitovaném (S_1) stavu na vzdálenosti, Spodní graf: příspěvek CT charakteru k celkové vlnové funkci.[11] b) Molekulární diagram tvorby excimeru

Je-li R<5 Å, CT stavy přispívají ke stabilizaci systému (pro naphthalene dimer je příspěvek v minimu 50%), systém získává povahu excimeru a výsledná funkce je kombinací CT a Frenkelova excitonu.

Větší stabilizaci komplexu lze vysvětlit pomocí molekulárního diagramu orbitalů uplatňujících se při excitaci (např. π orbitalů) na Obr. 3b. Při tvorbě dimeru A-B jsou π a π^* orbitaly výsledkem symetrické kombinace (π(A+B) a π^*(A+B)) a antisymetrické kombinace (π(A-B) a π^*(A-B)) orbitalů s energií nižší (vazebná, + kombinace) nebo vyšší (antivazebná, - kombinace) ve srovnání s orbitálními energiemi monomerů. V základním stavu jsou π(A+B) a π(A-B) plně obsazeny, a tedy dva elektrony obsadí stabilizující vazebný orbital a dva elektrony obsadí destabilizující antivazebný orbital. V celkové bilanci je příspěvek nulový a k stabilizaci přispívají pouze disperzní interakce. V excitovaném stavu obsadí tři elektrony stabilizující kombinaci a jeden elektron destabilizující kombinaci orbitalů, což vede k větší stabilitě oproti základnímu stavu.

1.4 Neadiabatické procesy

Pro popis neadiabatických jevů vedoucích k silné interakci mezi různými elektronovými konfiguracemi zúčastněných stavů je třeba zavést formalismus, který zohledňuje propojení pohybů jader a elektronů. Následující text stručně popisuje příslušný formalismus.

Časově nezávislá Schrödingerova rovnice pro systému má tvar

$$H^T\Psi^T(r,R) = E^T\Psi^T(r,R), \tag{4}$$

kde R je souřadnice jader, r je souřadnice elektronů a Hamiltonian H^T je definován

$$H^T(r,R) = T^N(R) + H(r,R), \tag{5}$$

kde $T^N(R)$ je operátor kinetické energie jader a $H(r,R)$ je elektronový Hamiltonián, který obsahuje kinetickou energii elektronů a Coulombickou interakci mezi částicemi. Řešením Schrödingerovy rovnice pro elektrony

$$H\Psi_I(r,R) = E_I(R)\Psi_I(r,R), \tag{6}$$

jsou vlastní funkce H, které mohou být použity k rozvoji celkové vlnové funkce ve formě

$$\Psi^T(r,R) = \sum \psi_I(r,R)\chi_I(r,R), \tag{7}$$

kde χ_I jsou rozvojové koeficienty. Použitím tohoto rozvoje lze po úpravách získat rovnici

$$[T^N + E_I]\chi_I - \sum\sum \frac{1}{2M_\alpha}\left(2f_{IJ}^\alpha \nabla_\alpha \chi_J + K_{IJ}^\alpha \chi_J\right) = E^T\chi_I, \tag{8}$$

kde α a J se vztahují ke stupňům volnosti jader a elektronů, respektivě. Členy K_{IJ} a f_{IJ} popisují interakci elektronických stavů I a J, vyplývají z operátoru kinetické energie jader operujícího na elektronické vlnové funkce $\psi_I(r,R)$ a mají tvar

$$f_{IJ}^{\alpha}(R) = \langle \psi_I(r,R) | \nabla_\alpha \psi_J(r,R) \rangle \tag{9}$$

$$K_{IJ}(R) = \sum \langle \psi_I(r,R) | \nabla_\alpha^2 \psi_J(r,R) \rangle, \tag{10}$$

kde ∇_α definuje gradient vzhledem k souřadnicím jader R.

Ve většině případů je systém popsán jedním elektronovým stavem, členy K_{IJ} a f_{IJ} jsou zanedbatelné a mohou tak být ignorovány, což vede k tzv. Born-Oppenheimrově aproximaci. V oblasti pseudo-křížení a křížení dvou PES musí být tyto členy zahrnuty. Vektor f_{IJ} je dominující, je měřítkem změny elektronické vlnové funkce vzhledem ke změnám souřadnic jader a je nepřímo úměrný rozdílu energií stavů I a J:

$$f_{IJ}(R) = \frac{\langle \psi_I | \nabla H | \psi_J \rangle}{E_I - E_J} \tag{11}$$

Je-li celková funkce Ψ^T rozvinuta v bázi vlastních funkcí celkového Hamiltoniánu H^T, je interakce mezi jednotlivými electronovými stavy zahrnuta v členu pro kinetickou energii jader T^N a nediagonální členy matice H^T jsou rovné nule. Taková representace se nazývá adiabatická. Alternativně lze použít diabatickou reprezentaci ϕ_I, ve které je interakce elektronických stavů vyjádřena nenulovými hodnotami nediagonálních členů matice Hamiltoniánu, který má tvar

$$H^{diab} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \tag{12}$$

a vlastní funkce mají tvar

$$E_{1,2} = \overline{H} \pm \sqrt{\Delta H^2 + H_{12}^2}, \tag{13}$$

kde $\overline{H} = (H_{11} + H_{22})/2$ a $\Delta H = (H_{11} - H_{22})/2$.

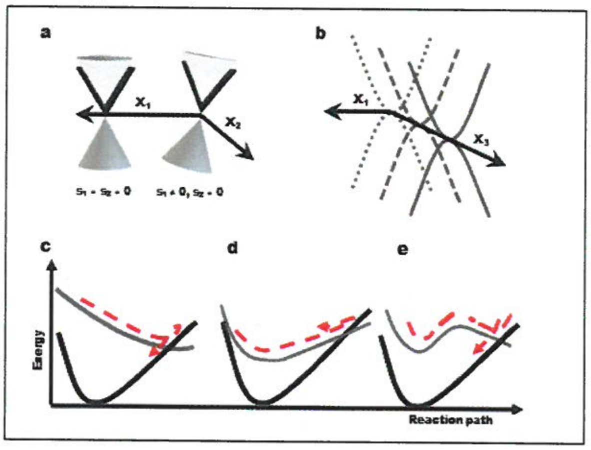
Pro degenerované hodnoty E_1 a E_2, tj. křížení dvou PES, musí být splněny podmínky $H_{11} - H_{22} = 0$ a $H_{12} = 0$. Tyto podmínky jsou splněny pro $\mathrm{N}^{\mathrm{int}} - 2$ podprostorů, kde $\mathrm{N}^{\mathrm{int}}$ je počet stupňů volnosti molekuly. Dvouatomová molekula má pouze jeden stupeň volnosti, a tak pro dva elektronické stavy o stejném spinu a symetrii tato podmínka nemůže být splněna, což vede k tzv. pravidlu o nekřížení stavů. Polyatomické molekuly splňují tuto podmínku pro $\mathrm{N}^{\mathrm{int}} - 2$ stupňů volnosti. Po jistých úpravách lze matici (12) přepsat v souřadnicích kónické intersekce:

$$H = (s_1 x + s_2 y)\mathbf{I}\begin{bmatrix} gx & hy \\ hy & -gx \end{bmatrix} \tag{14}$$

kde x a y odpovídají posunu ve směru vektoru gradientu energetického rozdílu **g** o normě g a vektoru mísení (coupling) **h** o normě h. Vektory **g** a **h** definují tzv. "branching space", podprostory, ve kterých je degenerace porušena, ostatní orthogonální podprostory definují tzv. "crossing seam". s_I a s_2 jsou projekcemi $(g_I+g_J)/2$ do roviny g-h, **I** je 2x2 jednotková matice. Vlastní funkce Hamiltoniánu (14) mají tvar

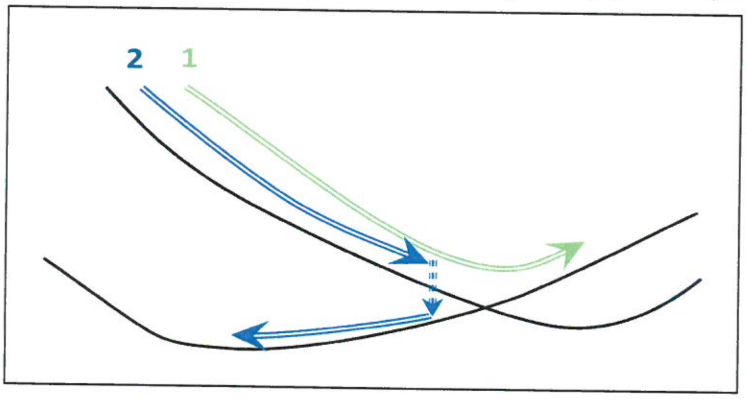
$$E_{1,2}(x,y) = s_1 x + s_2 y \pm \sqrt{(gx)^2 + (hy)^2} \tag{15}$$

Pomocí této rovnice je možné vykreslit PES obou stavů v okolí kónické intersekce, která má tvar dvojitého kužele podél dvou souřadnic (Obr. 4). Parametry g a h udávají tvar **CI**, parametry s_1, s_2 udávají její naklonění, kde nulové hodnoty s_1 a s_2 odpovídají vertikální **CI**. Obr. 4a znázorňuje tvar PES podél souřadnic x_1 a x_2, které definují "branching space"; Obr. 4b podél souřadnice x_3, která definuje "crossing seam". Tvar **CI** a jejího okolí má zásadní vliv na její efektivitu pro neadiabatický přechod, a tedy jeho pravděpodobnost. Obr. 4c-4e znázorňují příklady CI o různé efektivitě v důsledku charakteru PES v její blízkosti. V případě, kdy PES excitovaného stavu monotónně klesá k bodu křížení (Obr. 4c), je **CI** nejefektivnější a pravděpodobnost přechodu z jedné PES na druhou je velká. V situaci, kdy PES excitovaného stavu sleduje stoupající trend směrem k **CI** (Obr. 4d), se otevírá trajektorie zpět do minima excitovaného stavu. Odpovídající **CI** je odkloněna z vertikálního směru, je méně efektivní a přechod je méně pravděpodobný. Podobně, existence bariéry na PES excitovaného stavu na cestě k **CI** (Obr. 4e) způsobuje nižší pravděpodobnost přechodu.



Obr. 4. Kónické intersekce: (a) podél souřadnic x_1 a x_2, které definující "branching space", (b) podél souřadnice x_3, která definuje "crossing seam". Typy reakčních cest excitovaného stavu vedoucích k CI: (a) monotónně klesající, (d) stoupající z minima excitovaného stavu, (e) překonávající bariéru.

Popis procesů, při kterých BOA selhává, vyžaduje použití metod schopných zohlednit rozdělení populace mezi několik elektronových stavů. Jednou z nejpoužívanějších metod pro simulaci neadiabatických jevů je tzv. ´trajectory surface-hopping´ (TSH) metoda. V rámci této metody se struktura propaguje na jedné elektronické potenciální energetické ploše a při každém kroku stochastický algoritmus vyhodnocuje, ve kterém stavu bude trajektorie pokračovat (obr. 5). Tento postup se opakuje dokud není trajektorie dokončena. Vzhledem k stochastické povaze metody TSH je popis dynamiky plnohodnotný pouze v případě, že se uvažuje velký počet trajektorií.



Obr. 5. Dvě možné situace v TSH metodě: (1) – adiabatická trajektorie a (2) – neadiabatická trajektorie

1.5 Výpočetní metodika

Pro modelování systémů vyžadujících zahrnutí více elektronových konfigurací je třeba použít multi-konfigurační metodu (multi-configurational self-consistent field, MCSCF). V rámci této metody je celková vlnová funkce konstituována jako lineární kombinace Slaterových determinantů (SD), každý popisující jednu elektronovou konfiguraci. MCSCF tak kombinuje metodu konsistentního pole (Self Consistent Field, SCF) a konfigurační interakce (Configuration Interaction). Výsledná energie systému je získána optimalizací dvou typů rozvojových koeficientů: koeficientů c_{si} lineárního rozvoje atomových orbitalů χ_s při optimalizaci molekulových orbitalů φ_i (rovnice (16), MO-LCAO) v SCF

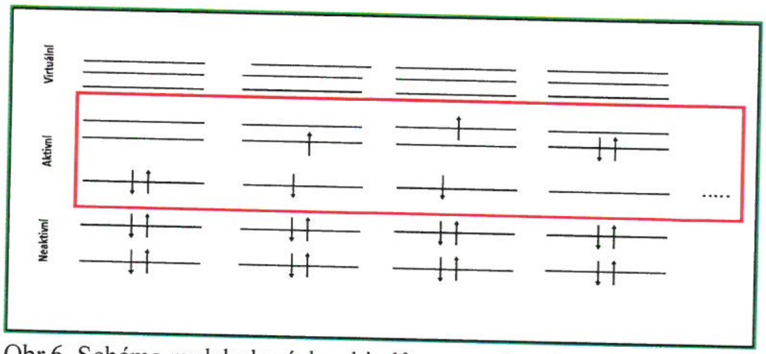
$$\varphi_i(1) = \sum_{s}^{M} c_{si}\chi_s(1), \tag{16}$$

(symbol (1) vyjadřuje, že každý atomový orbital, a tedy i molekulový orbital, závisí na souřadnicích jednoho elektronu (elektronu 1)) a koeficientů d_I lineárního rozvoje SD Φ_I v rozvoji konfigurační interakce

$$\Psi = \sum_{I} d_I \Phi_I . \tag{17}$$

Speciálním případem MCSCF metody je tzv. Complete Active Space Self-Consistent Field (CASSCF) metoda, ve které je omezen výběr elektronových konfigurací rozdělením orbitálního prostoru na neaktivní, aktivní a virtuální (Obr. 6). V neaktivním prostoru jsou orbitaly obsazeny dvěma elektrony (DOCC), v aktivních orbitalech tvořících tzv. aktivní prostor (AS) je možná jakákoliv elektronová konfigurace. Vybraný prostor je charakterizován počtem elektronů a orbitalů jako CAS(*n* elektronů, *m* orbitalů). Orbitaly v DOCC i AS jsou předmětem optimalizace.

Pro diskusi MCSCF metody je vhodné zavést pojem elektronové korelace, tedy vzájemného vlivu pohybu elektronů. Elektronová korelace bývá někdy rozdělována na dynamickou a statickou (nedynamickou). Dynamická korelace je důsledkem pohybu elektronů, nedynamická je spojena s nutností zahrnout do vlnové funkce systému více elektronových konfigurací, jak je popsáno v MCSCF metodě. Ostrá hranice mezi statickou a dynamickou korelací neexistuje.



Obr.6. Schéma molekulových orbitalů pro tvorbu aktivního prostoru.

2. Fotochemie nukleových kyselin

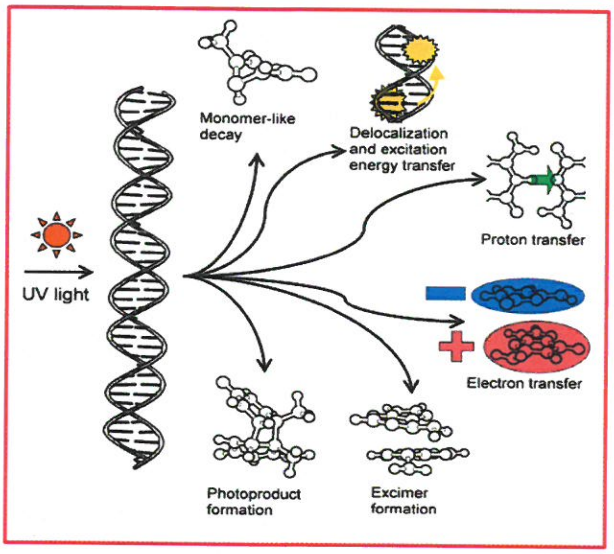
Komplexita chování nukleových kyselin (DNA i RNA) v excitovaném stavu představuje velkou výzvu pro experimentální i výpočetní chemiky studující tyto procesy. Všechny báze nukleových kyselin (nukleobáze) absorbují UV záření a jejich excitace může iniciovat fotoreakce, které ve svém důsledku mohou vést k poškození genetického kódu, tzv. mutacím.[12] Hlavním úkolem je pochopení relaxačních procesů následujících po elektronické excitaci. Vedle zářivé relaxace existuje v nukleových kyselinách několik nezářivých relaxačních procesů (obr. 7):

1) Lokalizace elektronické excitace na jedné bázi, po níž následuje relaxace v rámci tohoto monomeru
2) Delokalizace excitovaných stavů vedoucí k tvorbě excitonů
3) Přenos energie elektronické excitace.
4) Tvorba silně interagujícího komplexu - excimeru

5) Přenos elektronů nebo protonů mezi dvěma řetězci nebo v rámci jednoho řetězce

6) Vznik fotochemického produktu

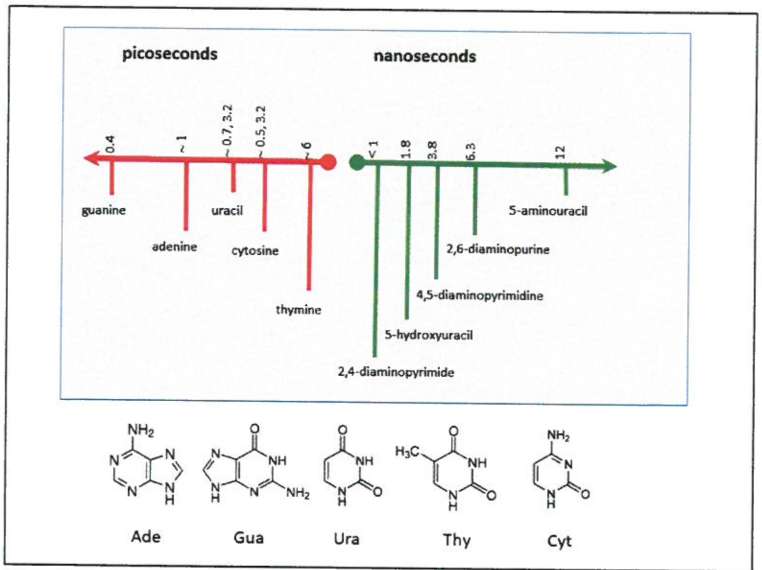
Reakce (6) neodpovídá situaci, kdy je zachována dříve zmíněná fotostabilita nukleových kyselin, a nebude proto dále diskutován.



Obr. 7. Relaxační mechanismy v molekulách nukleových kyselin

2.1 Fotochemie monomerů

Báze nukleových kyselin patří do skupiny aromatických heterocyklických sloučenin odvozených z pyrimidinu (cytosin, thymin a uracil) a purinu (adenin a guanin), chromophorů silně absorbující v UV oblasti. Díky přítomnosti heteroatomů jsou nízko položené excitované stavy výsledkem $\pi \rightarrow \pi^*$ a $n \rightarrow \pi^*$ přechodů, při vyšších energiích je možné dosáhnout také přechody do σ^* orbitalů. Variabilita excitovaných stavů mezi heterocykly založené na pyrimidinu a purinu je především ve stabilitě, tedy době života excitovaných stavů. Z obr. 8 je patrné, že společnou vlastností všech diskutovaných sloučenin vyskytujících se v nukleových kyselinách (nukleobází) je mimořádně krátká doba života excitovaných stavů, v řádu picosekund.[13] Zároveň je známo, že tyto báze mají velmi nízký kvantový výtěžek luminescence. Nukleobáze jsou tak schopné relaxovat do základního stavu nezářivými neadiabatickými mechanismy dříve než dojde k jejich chemické přeměně[14-16],Click or tap here to enter text.tj. vykazují fotostabilitu danou pravděpodobně evolučním tlakem v raném biotickém věku. Velmi malé modifikace v chemické struktuře způsobí změnu doby života excitovaných stavů v několika řádech. Např. substitucí vodíku v uracilu nebo methylové skupiny v thyminu v pozici C5 za OH nebo NH_2 skupinu se doba života prodlouží z pikosekund na nanosekundy (obr. 8).[17] Podobně i změna konformace má vliv na dobu života. Příkladem je cytosin a guanin, v kterých mají keto- formy kratší dobu života než enol formy. [13,18]



Obr. 8. Doby života excitovaných stavů bází nukleových kyselin a jejich modifikací

Výpočetní metody společně s ultrarychlou časově rozlišovanou spektroskopií[12,19,20] přispěly k značnému pokroku v pochopení neadiabatický procesů. Nicméně, interpretace experimentálních časově rozlišených spekter se v některých případech rozcházely v závislosti na použité metodice.[21] ***Autorka se podílela na komplexní studii všech nukleobází. Pomocí simulací neadiabatickou dynamikou na základě multi-referenčního popisu (CASSCF metodou) se podařilo získat sjednocující popis fotostability všech nukleobází[22-27], a na základě srovnání s jejich modifikacemi[17,28] objasnit mechanismus jejich relaxace.*** Výsledky těchto studií a jejich srovnání s experimentálními daty[21] jsou presentovány na obr. 9 a v Tab 1. a pro jednotlivé báze ukazují následující:

Adenin: Experimenty provedené při absorpční energie (E_{abs}) 250-270 nm ukazují, že doba života se zkracuje s rostoucí energií. Tento jev byl reprodukován pomocí simulací neadibatickou dynamikou, ve které byly doby života 0.77 ps a 0.63 ps pro E_{abs} 267nm a 250 nm. V obou případech relaxují všechny trajektorie s jedinou časovou konstantou, což ukazuje na homogenní relaxační mechanismus, A1, vedoucí k CI mezi $\pi\pi^*$ excitovaným a základním stavem (closed-shell, cs), charakterizované distorzí C_2 atomu z rovinu purinového cyklu.

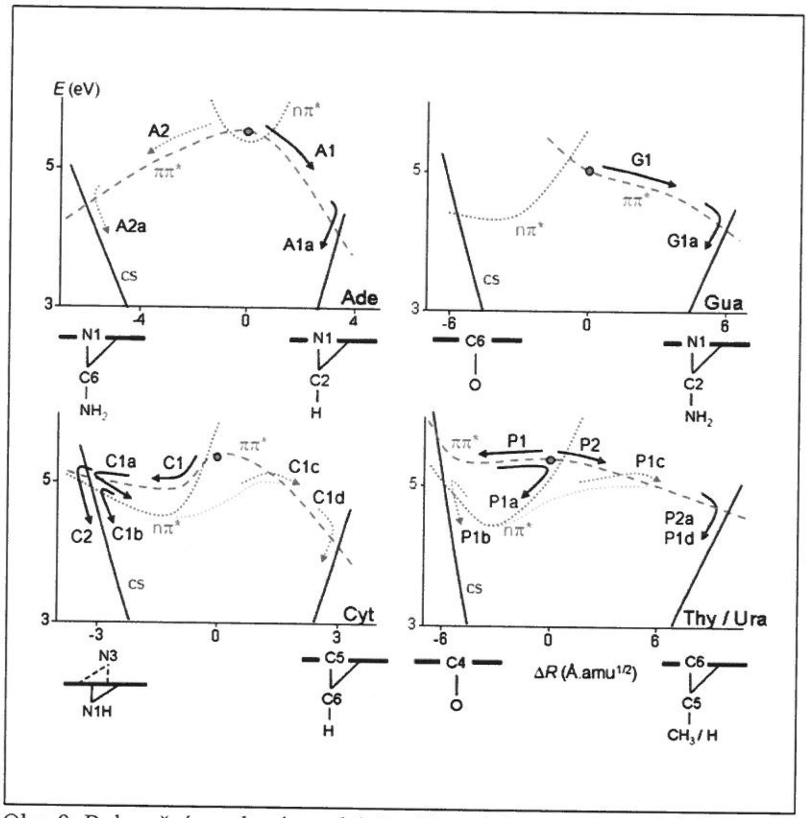
Guanin: z experimentálních studií prováděných s E_{abs} 267 nm byly v závislosti na způsobu fitování navrhnuty doby života 0.36 ps a 0.8 ps. Dynamické simulace reprodukovaly relaxaci s kratší dobou života. Také v tomto případě systém relaxuje s jedním relaxačním mechanismem G1 vedoucím k CI($\pi\pi^*$/cs), ve které je C_2 atom distortován z roviny purinového cyklu.

Cytosin: Experimentální studie provedené s $E_{abs} = 250$ nm poskytly doby života 0.8 ps a 3.2 ps. Experimenty s $E_{abs} = 267$ nm, v blízkosti centra prvního absorpčního bandu, nebyly publikovány. Podle dynamických simulací 74% populace relaxuje s časovou konstantou 0.53 ps, 13% s časovou konstantou 3.08 ps, což je v dobré shodě s výsledky experimentu. Simulace navíc ukázaly, že 13% populovaných stavů relaxuje v ultra-krátké době během 10 fs. Relaxační schéma cytosinu je mnohem komplexnější ve srovnání s guaninem a adeninem. Relaxační mechanismy sledované pro trajektorie s časovou konstantou 0.53 ps následují v 87% trajektorii s přechodem z $\pi\pi^*$ do $n\pi^*$ stavu přes quasiplanární CI (C1a). Z této CI se mechanismy dělí na dráhu C1b (58%), vedoucí ke quasiplanární CI na intersekci $n\pi^*$/cs, a na dráhu C1c vedoucí na C1d a dále k CI ($\pi\pi^*$/cs), charakterizované distorzí C6 atomu z roviny pyrimidinového kruhu, a následné relaxaci do základního stavu. Oba mechanismy probíhají na stejné časové škále. Minoritní frakce (13%) relaxuje během 10 fs na dráze C2.

Thymin: Představuje nukleobázi s nejdelší dobou života, v řádu nekolika ps, jak bylo pozorávno v experimentech s $E_{abs} = 267$ nm a 250 nm. Simulace provedené při těchto excitačních energiích ukázaly časové konstanty 2.3 ps v případě vyšších energií a 1.7 ps při nižších energiích. Po relaxaci do $S_1(n\pi^*)$ (P1a) stavu jsou dvě možnosti: 1. relaxace pomocí CI na intersekci $n\pi^*$/cs stavů (P1b), charakterizovanou distorzí O atomu z roviny pyrimidinového kruhu, 2. přechod do $\pi\pi^*$ stavu a dále k CI na intersekci $\pi\pi^*$/cs stavů (P1c a P1d), charakterizovanou distorzí C5 atomu z roviny pyrimidinového kruhu. Vzhledem k limitované době simulace 3 ps nelze jednoznačně predikovat, který mechanismus převažuje, i když nižší energie CI($\pi\pi^*$/cs) naznačuje, že P1c mechanismus převládá.

Uracil: Experimenty byly provedeny s $E_{abs} = 250$ nm, a to na dvou časových škálách, 0.5 ps a 2.4 ps. Při nižších energiích ($E_{abs} = 267$ nm) byla pozorována pouze relaxace s delší dobou života. Většina trajektorií (77%) simulována při nižší počáteční energii zrelaxovala během 1.8 ps z S_2 do S_1 stavu, další relaxace přesahovala čas simulace, tj. 2 ps. 23% trajektorií se zrelaxovalo do základního stavu během 0.74 ps. Podobné výsledky dávaly i simulace při vyšší E_{abs}, i když v kratším časovém úseku a s vyšší populací plně relaxujících trajektorií. Analýza trajektorií navrhla tři mechanismy relaxace. Většina populace (60%) relaxuje obdobným mechanismem jako thymin do $n\pi^*$ minima (P1a). Stejně jako u thyminu, následný relaxační mechanismus nebylo možno určit v rámci doby simulace. Druhý mechanismus, objevující se pro 31% trajektorií, který přispívá k deaktivaci s časovou konstantou 0.74 ps/0.66 ps, používá trajektorii podél $\pi\pi^*$ stavu (P2) k

CI($\pi\pi^*$/cs) charakterizované twistem podél C5C6 vazby. K deaktivaci probíhající na stejné časové škále přispívá i třetí mechanismus spojený s otevřením pyrimidinového kruhu mezi N3 a C4 atomy. Srovnání relaxačních mechanismů purinových a pyrimidinových bází ukazuje, že adenin a guanin



Obr. 9. Relaxační mechanismy bází nukleových kyselin získané pomocí neadiabické dynamické studie.[21]

představují fotodeaktivační mechanismus následující diabaticky $\pi\pi^*$ stav přímo a bez bariéry k CI na intersekci se základním stavem. K dosažení struktur lokalizovaných v CI je potřeba určitá koordinace v pohybech všech atomů, které ve svém výsledku vedou k distorzi purinového systému z roviny, vedoucí k poněkud odlišným časům pro adenin a guanin. Fotodynamika pyrimidinových bází je mnohem komplexnější a jejich doba života je větší, více než 0.5 ps. Důvodem je poměrně mělké minimum na PES $\pi\pi^*$ stavu způsobené existencí několika stavů $\pi\pi^*$ různého charakteru a delokalizovanými π orbitaly. Existence mělkého minima zpomaluje ´nalezení´ přímé $\pi\pi^*$ cesty. Detaily tvaru PES a energetických bariér pak určují další rysy dynamiky.

Dynamické simulace jednotlivých bází ukazují, že neexistuje žádná jedinečná fotodynamická deaktivace, nicméně lze definovat specifické vlastnosti pro určité relaxační cesty. Za zmínku stojí především déle trvající (několik ps) výskyt pyrimidinů, zvláště thyminu v S_2 minimu, tzv ´trapping´. Podobné zpomalovací mechanismy mohou s určitou pravděpodobností hrát roli v dalších fotoindukovaných procesech, např. tvorby pyrimidinových dimerů,[29] při které se předpokládá uplatnění tripletových excitovaných stavů. Singlet-tripletní přechod probíhá na větší časové škále a nemůže konkurovat relaxacím probíhajícím v rámci několika pikosekund, nicméně zpomalení podobná výše uvedenému trappingu by existenci tripletních stavů mohl umožnit. Podpůrným argumentem pro roli tripletních stavů v relaxaci nukleobází jsou studie naznačující, že v přítomnosti vody je aktivován $n\pi^*$ stav a z něj následně triplet.[30]

Bližší pochopení dynamického chování nukleobází přináší také studie alternativních systémů, které ukazují na vliv jednotlivých strukturálních parametrů, především distorzí z roviny kruhu nebo prodlužování vazeb, a jejich změn na pravděpodobnosti jednotlivých relaxačních cest, a tedy efektivity příslušných CI. Takové situace byly studovány např. na 2,4-diaminopyrimidinu a 2,6-diaminopurinu.[31] Podobně,velmi malé modifikace v chemické struktuře způsobí změnu doby života excitovaných stavů v několika řádech. Např. substitucí vodíku v uracilu nebo methylové skupiny v thyminu v pozici C5 za OH nebo NH_2 skupinu se doba života prodlouží z pikosekund na nanosekundy (obr. 8).[17]

Tab.1 Časové konstanty relaxace nukleobází

	λ(nm)	τ_1 (ps)	τ_2 (ps)		τ_3 (ps)		Reference[a]
		Exp	Exp	Simulated	Exp	Simulated	
Ade	250	< 0.05	0.75	0.63			1, 14
	267	0.10	1.0	0.77			2, 15-19
	277		~2				14,17
Gua	267	0.15	0.36 (0.86)[b]	0.28			2, 16
Thy	250	<0.05	0.49		6.4	>2.3	1
	267	0.11			5.1	>1.7	2,16
Ura	250	<0.05	0.53	0.65	2.4	>1.5	1
	267	0.13		0.74	1.1	>1.8	2,16
Cyt	250	<0.05	0.82		3.2		1
	267	0.16		0.53	1.86 (3.2)[b]	3.08	2,16

[a]reference v článku PNAS, [b]rozdílné hodnoty jsou dány rozdílnou fitovací procedurou v experimentu

2.2 Vliv okolních bází na absorpční spektra

Znalost povahy excitovaného stavu v nukleových kyselinách ve smyslu lokalizace excitace na monomeru nebo delokalizace je důležitá pro charakterizaci následného vývoje excitovaného systému. V molekulách nukleových kyselin jsou možné dva typy delokalizace, a to tvorba excitonu nebo CT excitovaných stavů.[11] ***Autorka se podílela na studiích kratších fragmentů***[32,33] ***ve vzájemných orientacích odpovídajících rozdílným konformacím DNA***, které ukázaly, že vliv okolních bází, a tedy i strukturních fluktuací, na excitační energie monomeru je minimální, podstatně ale ovlivňuje interakci transitních dipóvých momentů, tedy interakci mezi monomery.

Předmětem studií, na kterých se autorka podílela, bylo i ověření spolehlivosti výpočetních metod pro interpretaci absorpčních spekter. Bylo ukázáno, že v souladu s obecně známým faktem, že TDDFT metoda přeceňuje stabilitu CT stavů, metody založené na vlnové funkci ukazují, že tyto stavy jsou méně energeticky stabilní než lokalizované stavy. Navíc mají CT stavy ve srovnání s lokalizovanými stavy menší transitní dipolový moment (sílu oscilátoru), a tak menší příspěvek v absorpčních spektrech nukleových kyselin.[34]

2.3 Vliv okolních bází na procesy v excitovaných stavech

Efekty, které ovlivňují fotoaktivitu nukleobází, mohou být rozděleny na vnější (vliv okolního prostředí) a vnitřní (elektronické interakce mezi bázemi). Vzhledem k velikosti systému (až několik desítek bází) a požadavkům na výpočetní metodiku (multireferenční popis) je modelování těchto efektů výpočetně velmi náročné. Obvyklým přístupem je molekulová dynamika zahrnující neadiabatické efekty kombinující QM metody pro popis bází účastnících se excitace s MM metodami modelující okolní subsystém, tzv QM/MM metoda. ***Autorka se podílela na pracech studujích jak vliv ´stackových´ interakcí a vodíkových vazeb v rámci jednoho vlákna,***[26] ***tak vodíkových vazeb mezi bázemi sousedních vláken.***[27] Výsledky ukázaly, že zejména vodíkové vazby ovlivňují dosažitelnost CI purinových bází, charakterizovaných distorzí kruhu z roviny. Zatímco v prvním případě mají vodíkové vazby tendenci urychlovat relaxační proces podpořením této distorze, v druhém případě omezuje distorzi, a tím zabraňuje přístup k CI, jak bylo ukázáno na studiu dynamiky Gua v Cyt-Gua páru bazí v DNA. Vodíková vazba neovlivnila dobu života excitovaného Cyt, relaxace Gua se ale významně zpomalila. Příčinou je existence vodíkové vazby mezi kyslíkovým atomem C=O vazby cytosinu a vodíkovým atomem NH_2 skupiny gauninu, která omezuje dostupnost CI zodpovědnou za ultrakrátkou dobu života, kratší než 0.5 ps.

Tvorba excimerů/exciplexů, neutrálních i CT, je příkladem relaxace excitovaných stav v důsledku elektronových interakcí mezi bázemi, tedy vlivem vnitřních efektů. ***Autorka přispěla ke studiu těchto komplexů analýzou elektronické interakce z hlediska Coulombických a orbitálních překryvových členů.***[32,33] V těchto pracech bylo ukázáno, že elektronická interakce je výsledkem především Coulombických interakcí, zatímco orbitální překryv při vzdálenosti odpovídající vzdálenosti ve šroubovici DNA významně nepřispívá. Ukázalo se rovněž, že Coulmbické interakce mezi bázemi se vzájemnou orientací odpovídající konformaci A-DNA je větší než v případě která odpovídá konformaci B-DNA a že změny v excitačních energií způsobených nesymetrickými účinky jsou o řád větší než ty, které jsou způsobeny "čistými" elektronickými efekty. Vliv dimerizace včetně možné tvorby excimerů byly studovány také na xanthinových derivátech, systémech podobných nukleobázím.[35]

Výčet relaxačních mechanismů doplňuje tzv 'proton coupled electron transfer' (PCET) probíhající na jedné z vodíkových vazeb WC báze[36-41] předpovídající velmi rychlý proces deaktivace. Tento proces nebyl předmětem studia autorky, a proto není podrobněji diskutován.

3. Excitované stavy v kvantových tečkách

Od svého objevení se uhlíkové tečky (carbon dots, CD),[42] nanočástice na bázi uhlíku s alespoň jedním rozměrem menším než 10 nm, rozšířily do velké třídy nekovových fotoluminescenčních nanomateriálů. Jejich nespornou výhodou je nízká nebo nulová toxicita, biokompatibilita, dispergovatelnost v široké škále rozpouštědel, biologická odbouratelnost, nízké náklady, snadná a škálovatelná syntéza, předurčují CD k použití v mnoha oblastech životního prostředí. Díky své biokompatibilitě jsou CD ideálními kandidáty pro biosenzory v zobrazovacích metodách[43,44,] jako nosiče pro podávání léčiv a protinádorovou terapii.[45,46]

CD jsou malé fragmenty grafenu s konečnou velikostí, čímž vykazují na rozdíl od grafenu nenulový energetický gap mezi obsazenými a neobsazenými orbitaly, a tak jedinečné optické a elektronické vlastnosti, včetně výrazné fotoluminescence (PL). Díky variabilní velikosti, možnosti dopování heteroatomy, funkcionalizaci povrchu a přítomnosti různých typů defektů je možné dosáhnout PL od UV přes viditelnou až po blízkou infračervenou oblast a vykazovat různé PL charakteristiky, jako např. kvantový výtěžek, posuny v PL spektrech, atd. Za PL jsou zodpovědné tzv. jádra obsahující konjugované π-domény, celkové PL chování ale ovlivňuje také chemická struktura na okrajích CD. Elektronový gap s rostoucí velikostí klesá, což vede k červenému posunu emisního pásu. Jako u jiných systémů, i v CD je možná tvorba excimerů a excitonů nebo nezářivé relaxace a přechody na tripletní stavy, což výrazně ovlivňuje PL vlastnosti. Výčet faktorů, které mohou ovlivnit tyto vlastnosti doplňují další parametry, jako detaily struktury, chemické modifikace, způsob syntézy, reakční podmínky, atd. Popis PL vlastností a interpretace experimentálních dat tak představuje mimořádně komplikovaný problém, který je stále intenzině studován.[35]

CD jsou běžně modelovány pomocí polyaromatických uhlovodíků (polyaromatic hydrocarbons, PAH), tzv polyaceny, circumaceny a periaceny. V závislosti na struktuře a velikosti mohou mít vlnové funkce PAH v základním stavu uzavřenou nebo otevřenou (radikálovou) slupku a/nebo podíl excitovaných elektronických konfigurací. Charakteristickým rysem je přítomnost několika rezonančních struktur, jejichž příspěvky k vlnové funkci základního stavu rostou s velikostí systémů. Charakter vlnové funkce lze poměrně snadno a spolehlivě určit pomocí Clarova pravidla,[35,47-49] podle kterého má struktura s více aromatickými sextety (tzv. 'Clar' sextet) vyšší aromatickou stabilizační energii, díky čemuž je možné, že rádikálová struktura je stabilnější než struktura s uzavřenou slupkou (Kekulé struktura). Obr 10 ilustruje existenci dvou rezonančních struktur heptacenu (Obr 10a): Kekulé strukturu s uzavřenou slupkou a jedním ´Clar´ sexteterm a radikálovou strukturu s dvěma ´Clar´ sextety; a 3-2-3-periacenu (Obr. 10b): Kekulé strukturu s uzavřenou slupkou a dvěma ´Clar´ sextety a biradikálovou strukturou se čtyřmi ´Clar´ sextety. ***Autorka se podílela na dílčích problémech spojených s charakterizací těchto systémů v základním i excitovaném stavu, které jsou uvedeny v následujícím textu.***

3.1 Charakterizace excitovaných stavů

Radikálová povaha základního stavu spolu s příspěvky elektronových konfigurací s dvojnásobnou excitací pro větší systémy, jakož i multi-referenční povaha excitovaných stavů komplikuje výběr metodiky pro popis optických vlastností CD. Nejpoužívanější metodou pro tyto účely je jednoznačně metoda založená na tzv. ´time-dependent density functional theory´ (TDDFT). Uvedenou metodu, respektivě vhodnost jednotlivých funkcionálů, je nutné díky výše uvedeným problémům týkajících se základního stavu některých CD pečlivě testovat srovnáním s experimentem a metodami schopných správně popsat základní stav a následně poskytnout správné pořadí (ve smyslu energie) excitovaných stavů. ***Autorka se podílela na několika pracech, které se touto problematikou zabývají. Studie zahrnovaly charakterizaci excitovaných stavů serie polyacenů, naphtalenu (n=2, n je počet benzenových kruhů) až heptacenu (n=7),***[50] ***ve které byly detailně studovány statické i dynamické příspěvky korelační energie v jednotlivých excitovaných stavech.*** Pro větší systémy bylo ukázáno, že vzhledem ke kvazi-degenerovanému charakteru vlnových funkcí nemusí být běžně používané DFT metody vhodnou volbou a pro výpočty velkých PAH by se měly přednostně používat multireferenční přístupy.

Přesnost jednotlivých funkcionálů pro výpočty excitovaných stavů, především určení správného pořadí stavů jak lokalizovaných, tak CT stavů, bylo testováno na modelových systémech: pyrene, circum-1-pyrene, coronene, circum-1-coronene, and circum-2-coronene (obr 10c).[51] Absorpční spektra byly počítány multireferenčními metodami, ´density functional theory/multireference configuration interaction´ (DFT/MRCI), ´spectroscopy oriented configuration interaction´ (SORCI) a ´contracted-nelectron valence state perturbation theory to second order´ (NEVPT2), a jednoreferenčními metodami ´scaled opposite-spin-algebraic diagrammatic construction to second-order´ (SOS-ADC(2)), TD-B3LYP a TD-Coulomb-attenuating method-B3LYP (TD-CAM-B3LYP). Srovnáním s dostupnými experimentálními daty bylo ukázáno, že nejkonzistentnější metodou je DFT/MRCI a je doporučena pro menší systémy. Pro větší systémy, kde vzhledem k výpočetní náročnosti nelze použít multireferenční metody, jsou ze sledovaných metod nejvhodnější SOS-ADC(2) a CAM-B3LYP.

3.2 Efekt dopování heteroatomy na optické vlastnosti CD

Implementace heteroatomů do CD struktur je jedna z možností jak významně ovlivnit optoelektronické vlastnosti.[52] Např. v závislosti na koncentraci a poloze heteroatomu lze získat rozdílné typy posunů, tj. ke kratším i delším vlnovým délkám. Přítomnost heteroatomů také zvyšuje kvantový výtěžek fluorescence. Dopování N atomem, kterého lze dosáhnout během syntézy s použitím prekurzorů obsahujících atomy dusíku, je nejčastější.[53-55]

Autorka se podílela na studii zabývající se vlivu pozice N(H)-dopací pyrenu (1, obr. 10d). Byly zkoumány tzv. ′N-grafitic′ (2-4, obr. 10d), ′N-grafitic-edge′ (5 a 6, obr. 10d) a NH-pyridinové (7 – 9, obr. 10d) dopace na stabilitu elektronových struktur v základním stavu a vliv přítomnosti N atomů na optická spektra CD.[53,56] Analýza provedená na základě multireferenčních výpočtů a kvalitativně (teorie valenční vazby, Clarovo pravidlo, HOMA index pro hodnocení aromatičnosti atd.) umožnila racionalizovat relativní stability různých izomerů a také příslušné posuny v UV spektrech. V ′N-grafitic′ a ′N-grafitic-edge′ struktuře se počet π elektron ve srovnání s pyrenem zvyšuje o dva. V případě pyridinových pozic zůstává počet π elektronů nezměněn. V případě grafitického dopování se elektronický charakter řídí vzájemnou polohou atomů dusíku. Jsou-li N atomy lokalizovány na stejném typu alterujících atomů (uhlíkové atomy neoznačené nebo označené ′*′ v obr. 10d, struktuře **1**), má struktura silný biradikálový charakter a není možné zkonstruovat žádnou Kekulé strukturu. Přítomnost Clarova sextetu tento efekt ještě zesiluje. Bylo také zjištěno, že struktury s větší vzdáleností N atomů (ve smyslu počtu uhlíkových atomů mezi atomy dusíku) jsou stablilnější. Pyridinové substituce neovlivňují optická spektra ve srovnání s pyrenem na rozdíl od grafitických pozic, u kterých charakter absorpčních spekter závisí na výše diskutované (ne)radikálovém charakteru základního stavu. V případě radikálové povahy, tj. N atomy jsou v pozicích na stejném typu alterujících atomů a odděluje je tedy lichý počet atomů C, jsou S0 → S1 excitační energie v rozmezí od 0.5 – 1 eV, tj. spektrum je výrazně posunuto k nižším energiím (červený posun) do infračervené oblasti, zatímco grafitický N na okrajích GQDs může vyvolat buď červený nebo modrý posun.

Autorka se rovněž podílela na studiu vlivu přítomnosti F atomů na optická spektra CD.[57] V uvedené práci byl zkoumán vliv fluoru vázaného kovalentní vazbou, tj. na okrajích CD struktur, a vliv aniontem fluoru na absorpční a emisní spektra pyrenu a circum-1-pyrenu. Především byla zkoumána možnost dosažení červeného posunu ve spektrech a zvýšení intensity pásů. Studie byla provedena pomocí DFT/MRCI, ADC(2) a DFT/CAM-B3LYP metod. Jako v případě N-dopování, také vliv F-dopování závisí na pozici heteroatomu. Je-li F lokalizován nad aromatickým kruhem za vzniku záporně nabitého komplexu, dochází k výrazném posunu k nižším energiím v absorpčním i emisním spektru. Tyto změny jsou způsobeny vznikem nového excitovaného stavu s velkým podílem CT. Tento jev nebyl dříve pro komplexy tohoto typu zvažován. Kovalentní substituce nemají zásadní vliv na povahu absorpčních spekter. Navíc, optimalizace do minima excitovaného stavu ukazuje, že F má tendenci disociovat.

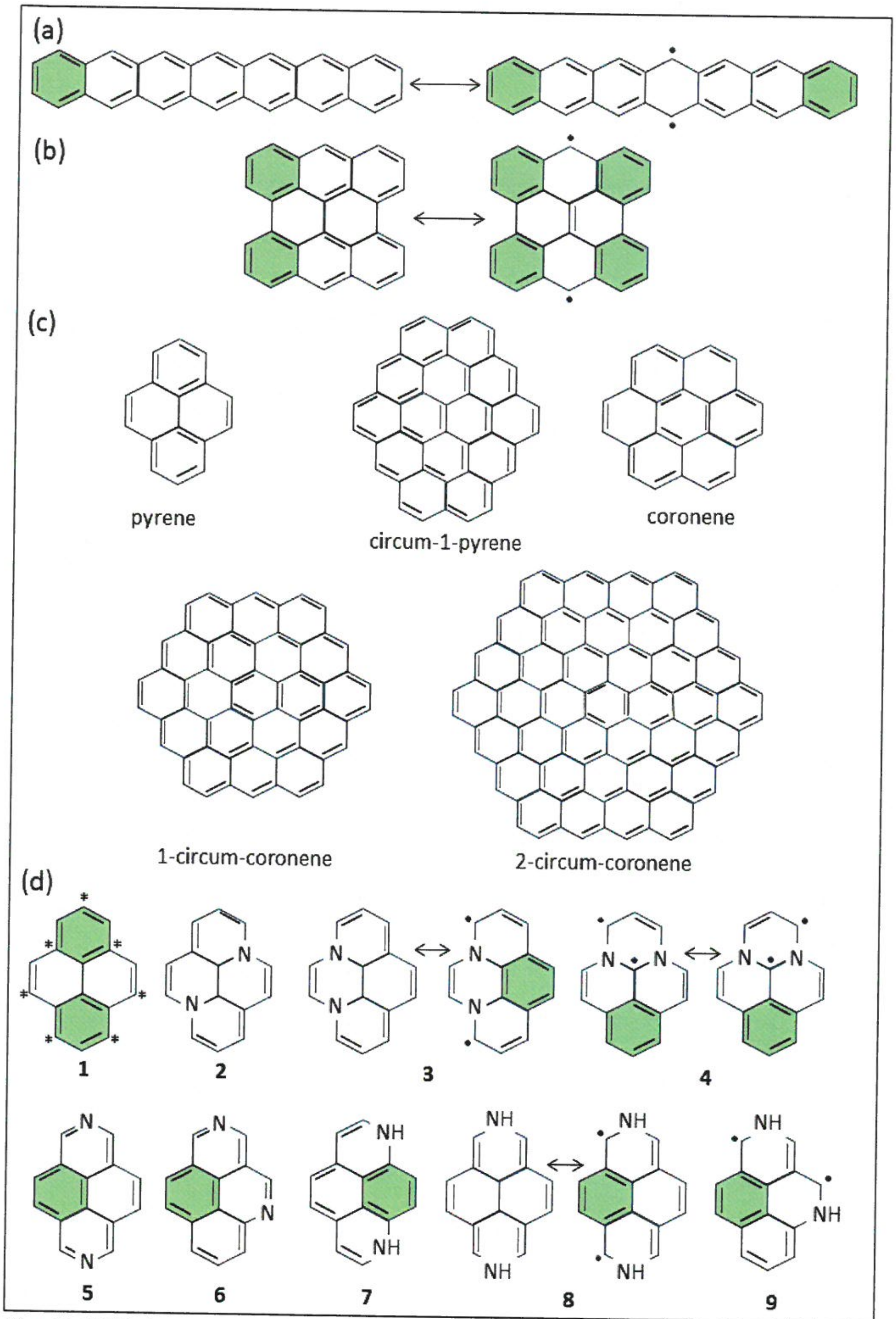
3.3 Interakce mezi PAH povrchy

V důsledku agregace mohou jednotlivé vrstvy PAH vzájemně interagovat pomocí tzv. ´stacking´ interakcí. Tyto interakce vyvolávají změny optických vlastností podobných těm pozorovaných v excimerech/exciplexech Jejich možné využití bylo naznačeno v několika studiích.[58,59]

K požadavkům na výpočetní metodu popsaných dříve pro monomery se přidávají další požadavky, především popis CT mezi jednotlivými monomery, popis elektronové korelaci na delší vzdálenost a ve srovnání se základním stavem větší polarizabilita systému ovlivňující interakce v excitovaném stavu. Pro popis excimerů/exciplexů je vhodnost standardní TD-DFT problematická, a to ze dvou důvodů: díky nesprávnému popisu disperzních interakcí nezbytných k získání přesných vazebných energií v základním a excitovaném stavu pro slabě vázané van der Waalsovy komplexy a díky nadhodnocené stabilitě stavů s CT charakterem.[60]

K modelování těchto asociátů se obvykle používají menší aromatické systémy (benzen, pyrene, perylene, atd.)[60,61] ***Autorka se podílela na studiu absorpčních a emisních spekter rozšířených modelů založených na pyrenu a coronenu,***[60,62] ***ve které byla rovněž testována spolehlivost TD-DFT (konkrétně TD-CAM-B3LYP) a ADC(2) metod na základě srovnání s DFT/MRCI výpočty a experimentálními daty.*** Studie ukázala, že obě jednoreferenční metody poskytují uspokojivou shodu s ´benchmark´ daty pro nižší-energetické excitované stavy, TD-CAM-B3LYP má ale tendenci podhodnocovat CT stavy, a tak nesprávně predikovat pořadí excitovaných stavů. I přes tyto problémy poskytuje TD-CAM-B3LYP rozumnou predikci změny v emisních spekter se zvětšujícím se počtem aromatických kruhů ve srovnání s DFT/MRCI (obr. 11). Rovněž extrapolace vedla k podobným hodnotám emisní energie pro nekonečně velké systémy ve srovnání s ADC(2) metodou, tj. 1.63 eV (760 nm, ADC(2)) a 1.77 eV (700 nm, TD-CAM_B3LYP), tedy hodnotám blížící se IČ oblasti.

Charakter emisních spekter, především otázka, zda je určován jedním chromophorem nebo agregáty více chromophorních skupin je jednou z hlavních otázek týkajících se optických vlastností CD. Zajímavým fenoménem pozorovaným experimentálně je výrazný rozdíl mezi absorpčními a emisními energiemi,[63,64] tzv. Stoke shift.



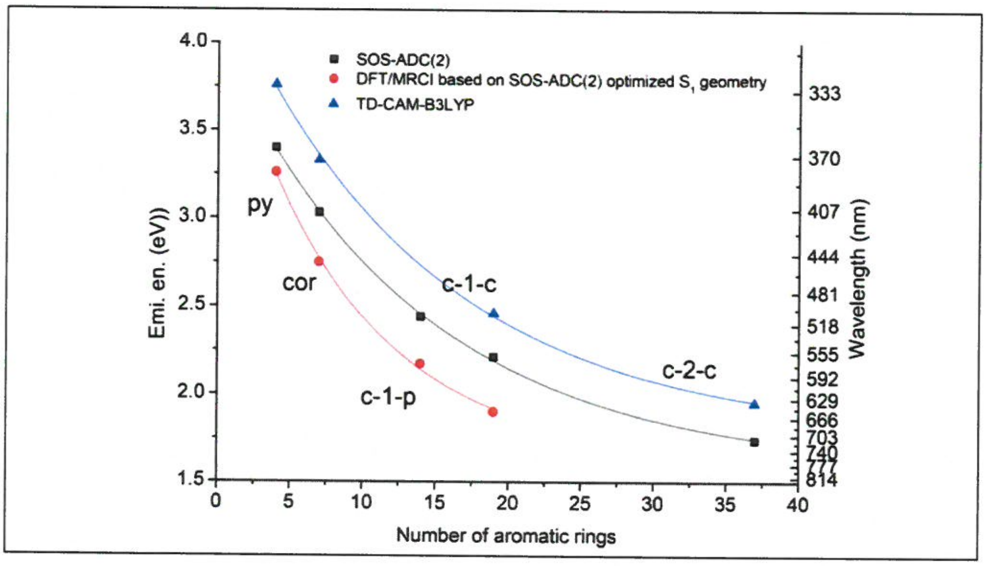
Obr. 10. Příklady rezonančních struktur polyaromatických uhlovodíků. Clar sextety jsou vyznačeny zeleně

Z Tab 2 publikované v práci,[62] ***na níž se autorka podílela***, je patrné, že hodnota Stokesova posunu klesá s rostoucí velikostí systému a dosahuje limitní hodnoty pro nekonečně velké systémy. To ukazuje, že experimentálně pozorované Stokesovy posuny nemohou být vysvětleny v rámci monomerů a jsou s největší pravděpodobností důsledkem agregátů, jak potvrzují také hodnoty získané pro dimery.

Tab. 2 Stokes shift (eV) pyrenu, circum-1-pyrenu, coronenu, circum-1-coronenu, circum-2-coronenu počítaný ADC(2) a TD-CAM-B3LYP metodami a def2-TZVP bází[a]

	TD-CAM-B3LYP	ADC(2)	
	Monomer	Monomer	Dimer
pyrene	0.27	0.31	0.96
circum-1-pyrene	--[b]	0.21	0.72
coronene	0.27	0.29	0.46
circum-1-coronene	0.16	0.17	0.53
circum-2-coronene	0.12	0.15	

[a]pro circum-2-coronene byla použita SVP báze, [b]nebylo vyhodnocováno v důsledku špatného řazení excitovaných stavů



Obr. 11 Závislost emisních energií na velikosti systémů polyaromatických uhlovodíků (počtu fúzovaných benzenových kruhů)

4. Shrnutí

Předkládaná práce shrnuje výsledky studií dvou biologicky relevantních systémů

1. Studium procesů v elektronicky excitovaných stavech bází nukleových kyselin, a to jak izolovaných, tak v prostředí tvořeném sousedními nukleobázemi. Tyto studie jsou významné k pochopení mimořádné fotostability nukleobází uplatňující se velmi pravděpodobně v raných fázích vzniku života, tak pochopení principů, kterými se nukleové báze chrání před svým poškozením vlivem, např. slunečního záření. Autorka se podílela na komplexní studii relaxačních mechanismů nukleobází jak v izolovaném stavu, tak interagujících s ostatními bázemi v rámci struktury nukleovách kyselin. K pochopení mechanismu přispěly rovněž

autorčiny práce popisující chování excitovaných stavů systémů, které představují modifikace nukleobází. V studiích byly použity metody založené na přesném *ab inito,* převážně multi-referenčním popisu systémů. Výsledky lze shrnout do následujících bodů:

i) Izolované nukleobáze relaxují rozdílnými mechanismy pro ty založené na purinu a pyrimidinu. Purinové báze mají kratší dobu života a při relaxaci do základního stavu sledují jeden $\pi\pi^*$ stav vedoucí bezbariérově ke kónické intersekci se základním stavem. Relaxace pyrimidinových bází je komplexnější v důsledku mělkého minima, která zpomaluje ´nalezení´ přímé $\pi\pi^*$ cesty. Další rozdíly dynamiky nukleobází jsou pak způsobeny detaily tvaru PES a energetických bariér.

ii) Modifikace nukleobází mají vliv na strukturní charakter kónických intersekcí, např. distorzí z roviny kruhu neb prodlužování vazeb, a a tak na dosažitelnost, a tedy efektivitu příslušných CI.

iii) Okolní báze ovlivňují relaxační mechanismus jednak možnou tvorbou eximerů, ve kterých se uplatňují tzv. ´stacking´ interakce v rámci jednoho vlákna nukleových kyselin, tak interakcemi v rámci dvou vláken, které mohou omezit strukturální změny nutné k dosažení příslušné kónické intersekce.

2. Charakterizace uhlíkových teček, které vzhledem ke své netoxicitě a biologické kompatibilitě a zároveň výrazným fotoluminescenčním vlastnostem představují materiály s vysokým potenciálem využití v medicinálních oborech. Na druhou stranu, v důsledku komplexního charakteru těchto systémů představuje racionalizace jejich fotoluminescenčních vlastností stále velkou výzvu. Výpočetní modelování je komplikováno také velikostí uvedených systémů, a tak problémy s použitím přesných výpočetních metod. Studie provedené na souboru polyaromatických uhlovodíků a jejich modifikovaných systémech ukázaly:

i) Bezpečnou metodou pro spolehlivou interpretaci absorpčních spekter je multireferenční metoda schopná správně popsat jak ´statickou´, tak ´dynamickou´ korelaci. Použití TD-DFT metod vyžaduje pečlivé testování funkcionálů.

ii) Vliv přítomnosti dopantů na povahu absorpčních spekter, konkrétně výrazných posunů k nižším absorpřním energiím byl vysvětlen na základě analýzy elektronové povahy základního stavu u N-dopovaných PAH a na přítomností nově vzniklých ´charge-transfer excitovaných stavů u F-dopovaných PAH.

iii) Bylo ukázáno, že experimentálně pozorovaný posun mezi absorpčními a emisními pásy je s největší pravděpodobností způsoben přítomností agregátů vzniklých mezi chromophorními skupinami.

Reference (publikace autorky vztahující se k tématu habilitace jsou zvýrazněny tučně)

(1) Lischka, H.; Nachtigallová, D.; Aquino, A. J. A.; Szalay, P. G.; Plasser, F.; MacHado, F. B. C.; Barbatti, M. Multireference Approaches for Excited States of Molecules. *Chem Rev*, 2018, pp 7293–7361.

(2) Negri, F.; Zgierski, M. ON THE VIBRONIC STRUCTURE OF THE S0[--]S1 TRANSITIONS IN AZULENE. *J. Chem. Phys.* **1993**, *99* (6), 4318–4326.

(3) Dierksen, M.; Grimme, S. Density Functional Calculations of the Vibronic Structure of Electronic Absorption Spectra. *J. Chem. Phys* **2004**, *120* (8), 3544–3554.

(4) Mebel, A. M.; Hayashi, M.; Liang, K. K.; Lin, H. S. Ab Initio Calculations of Yibronic Spectra and Dynamics for Small Polyatomic Molecules: Role of Duschinsky Effect. *J. Phys. Chem. A* **1999**, *103* (50), 10674–10690.

(5) *Photoinduced Processes in Nucleic Acids*; Barbatti, M., Borin, A., Ullrich, S., Eds.; Springer: Cham, 2014; Vol. 355, 356.

(6) Barbatti, M.; Shepard, R.; Lischka, H. *Computational and Methodological Elements for Nonadiabatic Trajectory Dynamics Simulations of Molecules. In Conical Intersections: Theory, Computation and Experiment*, Adv Ser Phys Chem.; Domcke, W., Yarkony, D. R., Köppel, H., Eds.; World Scientific: Köppel, H, 2011; Vol. 15.

(7) *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, Adv Ser Phys Chem.; Domcke, W., Yarkony, D., Köppel, H., Eds.; World Scientific: Singapore, 2004; Vol. 15.

(8) *Conical Intersections: Theory, Computation and Experiment*, Adv Ser Phys Chem.; Domcke, W., Yarkony, D. R., Köppel, H., Eds.; World Scientific: Singapore, 2011; Vol. 17.

(9) Petrenko, T.; Neese, F. Analysis and Prediction of Absorption Band Shapes, Fluorescence Band Shapes, Resonance Raman Intensities, and Excitation Profiles Using the Time-Dependent Theory of Electronic Spectroscopy. *J. Chem. Phys.* **2007**, *127*, 164319.

(10) Stolow, A.; Bragg, A. E.; Neumark, D. M. Femtosecond Time-Resolved Photoelectron Spectroscopy. *Chem Rev* **2004**, *104* (4), 1719–1757.

(11) Plasser, F.; Aquino, A. J. A.; Lischka, H.; Nachtigallová, D. Electronic Excitation Processes in Single-Strand and Double-Strand DNA: A Computational Approach. *Top Curr Chem* 2015, *356*, 1–38.

(12) Pfeifer, G.; You, Y.; Besaratinia, A. Mutations Induced by Ultraviolet Light. *MUTATION RESEARCH-FUNDAMENTAL AND MOLECULAR MECHANISMS OF MUTAGENESIS* **2005**, *571* (1), 19–31.

(13) **Kleinermanns, K.; Nachtigallová, D.; de Vries, M. S. Excited State Dynamics of DNA Bases. *Int. Rev. Phys. Chem.* June 2013, pp 308–342.**

(14) Ullrich, S.; Schultz, T.; Zgierski, M. Z.; Stolow, A. Electronic Relaxation Dynamics in DNA and RNA Bases Studied by Time-Resolved Photoelectron Spectroscopy. *Phys Chem Chem Phys* **2004,** *6* (10), 2796–2801.

(15) Canuel, C.; Mons, M.; Piuzzi, F.; Tardivel, B.; Dimicoli, I.; Elhanine, M. Excited States Dynamics of DNA and RNA Bases: Characterization of a Stepwise Deactivation Pathway in the Gas Phase. *J. Chem. Phys* **2005,** *122* (7).

(16) Blancafort, L.; Cohen, B.; Hare, P. M.; Kohler, B.; Robb, M. A. Singlet Excited-State Dynamics of 5-Fluorocytosine and Cytosine: An Experimental and Computational Study. *J. Phys. Chem A* **2005,** *109* (20), 4431–4436: 074316

(17) **Nachtigallová, D.; Lischka, H.; Szymczak, J. J.; Barbatti, M.; Hobza, P.; Gengeliczki, Z.; Pino, G.; Callahan, M. P.; De Vries, M. S. The Effect of C5 Substitution on the Photochemistry of Uracil. *Phys Chem Chem Phys* 2010, *12* (19).4924-4933.**

(18) Nakayama, A.; Harabuchi, Y.; Yamazaki, S.; Taketsugu, T. Photophysics of Cytosine Tautomers: New Insights into the Nonradiative Decay Mechanisms from MS-CASPT2 Potential Energy Calculations and Excited-State Molecular Dynamics Simulations. *Phys Chem Chem Phys* **2013,** *15* (29), 12322–12339.

(19) Coulondre, C.; Miller, J. H. *Genetic Studies of the Zac Repressor IV. Mutagenic Specificity in the ZucI Gene of Escherichiu Coli*; *J.Mol. Biol.* **1977**; Vol. 117(3), 577-606.

(20) Perun, S.; Sobolewski, A. L.; Domcke, W. Ab Initio Studies on the Radiationless Decay Mechanisms of the Lowest Excited Singlet States of 9H-Adenine. *J Am Chem Soc* **2005,** *127* (17), 6257–6265.

(21) **Barbatti, M.; Aquino, A. J. A.; Szymczak, J. J.; Nachtigallová, D.; Hobza, P.; Lischka, H. Relaxation Mechanisms of UV-Photoexcited DNA and RNA Nucleobases. *Proc Natl Acad Sci U S A* 2010, *107* (50), 21453-21458.**

(22) **Szymczak, J. J.; Barbatti, M.; Soo Hoo, J. T.; Adkins, J. A.; Windus, T. L.; Nachtigallova, D.; Lischka, H. Photodynamics Simulations of Thymine: Relaxation into the First Excited Singlet State. *J. Phys. Chem A* 2009, *113* (45), 12686-12693.**

(23) **Nachtigallova, D.; Aquino, A. J. A.; Szymczak, J. J.; Barbatti, M.; Hobza, P.; Lischka, H. Nonadiabatic Dynamics of Uracil: Population Split among Different Decay Mechanisms. *J. Phys. Chem A* 2011, *115* (21), 5247–5255.**

(24) **Barbatti, M.; Szymczak, J. J.; Aquino, A. J. A.; Nachtigallov, D.; Lischka, H. The Decay Mechanism of Photoexcited Guanine - A Nonadiabatic Dynamics Study. *J. Chem. Phys* 2011, *134* (1):014304.**

(25) **Zelený, T.; Hobza, P.; Nachtigallová, D.; Ruckenbauer, M.; Lischka, H. Photodynamics of the Adenine Model 4-Aminopyrimidine Embedded within Double Strand of DNA. *Collect Czech Chem Commun* 2011, *76,* 631-643.**

(26) **Nachtigallová, D.; Zelený, T.; Ruckenbauer, M.; Müller, T.; Barbatti, M.; Hobza, P.; Lischka, H. Does Stacking Restrain the Photodynamics of Individual Nucleobases-. *J Am Chem Soc* 2010, *132* (24), 8261–8263.**

(27) **Zelený, T.; Ruckenbauer, M.; Aquino, A. J. A. A.; Müller, T.; Lankaš, F.; Dršata, T.; Hase, W.; Nachtigallova, D.; Lischka, H. Strikingly Different Effects of Hydrogen Bonding on the Photodynamics of Individual Nucleobases in DNA: Comparison of Guanine and Cytosine. *J Am Chem Soc* 2012, *134* (33), 13662–13669.**

(28) **Nachtigallová, D.; Barbatti, M.; Szymczak, J. J.; Hobza, P.; Lischka, H. The Photodynamics of 2,4-Diaminopyrimidine in Comparison with 4-Aminopyrimidine: The Effect of Amino-Substitution. *Chem Phys Lett* 2010, *497* (1–3), 129-134.**

(29) Kwok, W. M.; Ma, C.; Phillips, D. L. A Doorway State Leads to Photostability or Triplet Photodamage in Thymine DNA. *J Am Chem Soc* **2008,** *130* (15), 5131–5139.

(30) Hare, P. M.; Crespo-Herná Ndez, C. E.; Kohler, B. *Internal Conversion to the Electronic Ground State Occurs via Two Distinct Pathways for Pyrimidine Bases in Aqueous Solution*; 2006. www.pnas.org/cgi/content/full/.

(31) **Gengeliczki, Z.; Callahan, M. P.; Svadlenak, N.; Pongor, C. I.; Sztáray, B.; Meerts, L.; Nachtigallová, D.; Hobza, P.; Barbatti, M.; Lischka, H.; de Vries, M. S. Effect of Substituents on the Excited-State Dynamics of the Modified DNA Bases 2,4-Diaminopyrimidine and 2,6-Diaminopurine. *Phys Chem Chem Phys* 2010, *12* (20), 5375–5388.**

(32) **Nachtigallová, D.; Hobza, P.; Ritze, H.-H. Electronic Splitting in the Excited States of DNA Base Homodimers and -Trimers: An Evaluation of Short-Range and Coulombic Interactions.** *Phys Chem Chem Phys* **2008, *10* (37), 5689-5697.**

(33) **Ritze, H.-H.; Hobza, P.; Nachtigallová, D. Electronic Coupling in the Excited Electronic State of Stacked DNA Base Homodimers. *Phys Chem Chem Phys* 2007, *9* (14), 1672-1675.**

(34) Aquino, A. J. A.; Nachtigallova, D.; Hobza, P.; Truhlar, D. G.; Hättig, C.; Lischka, H. The Charge-Transfer States in a Stacked Nucleobase Dimer Complex: A Benchmark Study. *J Comput Chem* 2011, *32* (7), 1217-1227.

(35) Nachtigallová, D.; Aquino, A. J. A.; Horn, S.; Lischka, H. The Effect of Dimerization on the Excited State Behavior of Methylated Xanthine Derivatives: A Computational Study. *Photochem. Photobiol. Sci* 2013, *12* (8), 1498-1508.

(36) Sobolewski, A. L.; Domcke, W. Ab Initio Studies on the Photophysics of the Guanine-Cytosine Base Pair. *Phys Chem Chem Phys* **2004**, *6* (10), 2763–2771.

(37) Perun, S.; Sobolewski, A. L.; Domcke, W. Role of Electron-Driven Proton-Transfer Processes in the Excited-State Deactivation of the Adenine-Thymine Base Pair. *J. Phys. Chem A* **2006**, *110* (29), 9031–9038

(38) Sobolewski, A. L.; Domcke, W.; Hä, C. *Tautomeric Selectivity of the Excited-State Lifetime of Guaninecytosine Base Pairs: The Role of Electron-Driven Proton-Transfer Processes*; 2005; Vol. 13. www.pnas.org

(39) Schwalb, N.K.; Temps, F. Ultrafast Electronic Relaxation in Guanosine Is Promoted by Hydrogen. *J Am Chem Soc* **2007,** *129(30),* 9272-9273.

(40) Groenhof, G.; Schäfer, L. V.; Boggio-Pasqua, M.; Goette, M.; Grubmüller, H.; Robb, M. A. Ultrafast Deactivation of an Excited Cytosine-Guanine Base Pair in DNA. *J Am Chem Soc* **2007**, *129* (21), 6812–6819.

(41) Markwick, P. R. L.; Doltsinis, N. L. Ultrafast Repair of Irradiated DNA: Nonadiabatic Ab Initio Simulations of the Guanine-Cytosine Photocycle. *J. Chem. Phys* **2007**, *126* (17):175102

(42) Xu, X.; Ray, R.; Gu, Y.; Ploehn, H. J.; Gearheart, L.; Raker, K.; Scrivens, W. A. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. *J Am Chem Soc* **2004**, *126* (40), 12736–12737.

(43) Suvarnaphaet, P.; Pechprasarn, S. Graphene-Based Materials for Biosensors: A Review. *Sensors* **2017** *17(100)*:2161

(44) Chauhan, N.; Maekawa, T.; Nair, D.; Kumar, S.; Graphene Based Biosensors-Accelerating Medical Diagnostics to New-Dimensions. *J. Mater. Res.* **2017**, *32(15),* 2860-2862.

(45) Li, K.; Liu, W.; Ni, Y.; Li, D.; Lin, D.; Su, Z.; Wei, G. Technical Synthesis and Biomedical Applications of Graphene Quantum Dots. *J. Mater. Chem. B* **2017**, *5*, 4811.

(46) Iannazzo, D.; Ziccarelli, I.; Pistone, A. Graphene Quantum Dots: Multifunctional Nanoplatforms for Anticancer Therapy. *J Mater Chem B* **2017**, *5* (32), 6471–6489.

(47) Plasser, F.; Pašalic, H.; Gerzabek, M. H.; Libisch, F.; Reiter, R.; Burgdçrfer, J.; Müller, T.; Shepard, R.; Lischka, H.. The Multiradical Character of One-and Two-Dimensional Graphene Nanoribbons**. *Angew. Chem. Int. Ed* **2013**, *52*, 2581–2584.

(48) Horn, S.; Plasser, F.; Mü, T.; Libisch, F.; Burgdörfer, J.; Lischka, H. A Comparison of Singlet and Triplet States for One-and Two-Dimensional Graphene Nanoribbons Using Multireference Theory. *Theor. Chem. Acc.* **2014,** *133:* 1511.

(49) Yang, Y.; Davidson, E. R.; Yang, W. Nature of Ground and Electronic Excited States of Higher Acenes. *Proc Natl Acad Sci U S A* **2016**, *113* (35), E5098–E5107.

(50) Bettanin, F.; Ferrão, L. F. A.; Pinheiro, M.; Aquino, A. J. A.; Lischka, H.; Machado, F. B. C.; Nachtigallova, D. Singlet La and Lb Bands for N-Acenes (N = 2-7): A CASSCF/CASPT2 Study. *J Chem Theory Comput* 2017, *13* (9), 4297–4306.

(51) Shi, B.; Nachtigallová, D.; Aquino, A. J. A.; Machado, F. B. C.; Lischka, H. High-Level Theoretical Benchmark Investigations of the UV-Vis Absorption Spectra of Paradigmatic Polycyclic Aromatic Hydrocarbons as Models for Graphene Quantum Dots. *J. Chem. Phys* 2019, *150* (12):124302.

(52) Sk, M. A.; Ananthanarayanan, A.; Huang, L.; Lim, K. H.; Chen, P. Revealing the Tunable Photoluminescence Properties of Graphene Quantum Dots. *J Mater Chem C Mater* **2014**, *2* (34), 6954–6960.

(53) Holá, K.; Sudolská, M.; Kalytchuk, S.; Nachtigallová, D.; Rogach, A. L.; Otyepka, M.; Zbořil, R. Graphitic Nitrogen Triggers Red Fluorescence in Carbon Dots. *ACS Nano* 2017, *11* (12), 12402–12410.

(54) Kozák, O.; Sudolská, M.; Pramanik, G.; Cígler, P.; Otyepka, M.; Zbořil, R. Photoluminescent Carbon Nanostructures. *Chemistry of Materials* **2016**, *28* (12), 4085–4128.

(55) Langer, M.; Paloncýová, M.; Medveď, M.; Pykal, M.; Nachtigallová, D.; Shi, B.; Aquino, A. J. A.; Lischka, H.; Otyepka, M. Progress and Challenges in Understanding of Photoluminescence Properties of Carbon Dots Based on Theoretical Computations. *Applied Materials Today*. Elsevier Ltd March 1, 2021.

(56) Shao, X.; Aquino, A. J. A.; Otyepka, M.; Nachtigallová, D.; Lischka, H. Tuning the UV Spectrum of PAHs by Means of Different N-Doping Types Taking Pyrene as Paradigmatic Example: Categorization: Via Valence Bond Theory and High-Level Computational Approaches. *Phys Chem Chem Phys* 2020, *22* (38), 22003–22015.

(57) Liu, B.; Aquino, A.; Nachtigallova, D.; Lischka, H. Doping Capabilities of Fluorine on the UV Absorption and Emission Spectra of Pyrene-Based Graphene Quantum Dots. *J Phys Chem A 0* (0), null-null. https://doi.org/10.1021/acs.jpca.0c08694.

(58) Vollbrecht, J. Excimers in Organic Electronics. *New Journal of Chemistry* **2018**, *42* (14), 11249–11254.

(59) Wang, J.; Zhang, F.; Wang, Y.; Yang, Y.; Liu, X. Efficient Resistance against Solid-State Quenching of Carbon Dots towards White Light Emitting Diodes by Physical Embedding into Silica. **2017**.

(60) Shi, B.; Nachtigallová, D.; Aquino, A. J. A.; Machado, F. B. C.; Lischka, H. Excited States and Excitonic Interactions in Prototypic Polycyclic Aromatic Hydrocarbon Dimers as Models for Graphitic Interactions in Carbon Dots. *Phys Chem Chem Phys* 2019, *21* (18), 9077–9088.

(61) Sarkar, S.; Sudolská, M.; Dubecký, M.; Reckmeier, C. J.; Rogach, A. L.; Zbořil, R.; Otyepka, M. Graphitic Nitrogen Doping in Carbon Dots Causes Red-Shifted Absorption. *J. Phys. Chem C* **2016**, *120* (2), 1303–1308.

(62) Shi, B.; Nachtigallová, D.; Aquino, A. J. A.; Machado, F. B. C.; Lischka, H. Emission Energies and Stokes Shifts for Single Polycyclic Aromatic Hydrocarbon Sheets in Comparison to the Effect of Excimer Formation. *J. Phys. Chem Lett* 2019, *10* (18), 5592–5597.

(63) Malyukin, Y.; Viagin, O.; Maksimchuk, P.; Dekaliuk, M.; Demchenko, A. Insight into the Mechanism of the Photoluminescence of Carbon Nanoparticles Derived from Cryogenic Studies. *Nanoscale* **2018**, *10*, 9320.

(64) Gude, V.; Das, A.; Chatterjee, T.; Mandal, P. K. Cite This. *Phys. Chem. Chem. Phys* **2827**, *18*, 28274.

Příloha

Seznam publikací autorky týkající se habilitační práce (titulní strana)

1. Lischka, H.; Nachtigallová, D.; Aquino, A. J. A.; Szalay, P. G.; Plasser, F.; MacHado, F. B. C.; Barbatti, M. Multireference Approaches for Excited States of Molecules. *Chem Rev*, 2018, pp 7293–7361
2. Plasser, F.; Aquino, A. J. A.; Lischka, H.; Nachtigallová, D. Electronic Excitation Processes in Single-Strand and Double-Strand DNA: A Computational Approach. *Top Curr Chem* 2015, *356*, 1–38
3. Kleinermanns, K.; Nachtigallová, D.; de Vries, M. S. Excited State Dynamics of DNA Bases. *Int. Rev. Phys. Chem*. June 2013, pp 308–342
4. Nachtigallová, D.; Lischka, H.; Szymczak, J. J.; Barbatti, M.; Hobza, P.; Gengeliczki, Z.; Pino, G.; Callahan, M. P.; De Vries, M. S. The Effect of C5 Substitution on the Photochemistry of Uracil. *Phys Chem Chem Phys* 2010, *12* (19).4924-4933
5. Barbatti, M.; Aquino, A. J. A.; Szymczak, J. J.; Nachtigallová, D.; Hobza, P.; Lischka, H. Relaxation Mechanisms of UV-Photoexcited DNA and RNA Nucleobases. *Proc Natl Acad Sci U S A* 2010, *107* (50), 21453-21458
6. Szymczak, J. J.; Barbatti, M.; Soo Hoo, J. T.; Adkins, J. A.; Windus, T. L.; Nachtigallova, D.; Lischka, H. Photodynamics Simulations of Thymine: Relaxation into the First Excited Singlet State. *J. Phys. Chem A* 2009, *113* (45), 12686-12693
7. Nachtigallova, D.; Aquino, A. J. A.; Szymczak, J. J.; Barbatti, M.; Hobza, P.; Lischka, H. Nonadiabatic Dynamics of Uracil: Population Split among Different Decay Mechanisms. *J. Phys. Chem A* 2011, *115* (21), 5247–5255
8. Barbatti, M.; Szymczak, J. J.; Aquino, A. J. A.; Nachtigallov, D.; Lischka, H. The Decay Mechanism of Photoexcited Guanine - A Nonadiabatic Dynamics Study. *J. Chem. Phys* 2011, *134* (1):014304
9. Zelený, T.; Hobza, P.; Nachtigallová, D.; Ruckenbauer, M.; Lischka, H. Photodynamics of the Adenine Model 4-Aminopyrimidine Embedded within Double Strand of DNA. *Collect Czech Chem Commun* 2011, *76,* 631-643
10. Nachtigallová, D.; Zelený, T.; Ruckenbauer, M.; Müller, T.; Barbatti, M.; Hobza, P.; Lischka, H. Does Stacking Restrain the Photodynamics of Individual Nucleobases-. *J Am Chem Soc* 2010, *132* (24), 8261–8263
11. Zelený, T.; Ruckenbauer, M.; Aquino, A. J. A. A.; Müller, T.; Lankaš, F.; Dršata, T.; Hase, W.; Nachtigallova, D.; Lischka, H. Strikingly Different Effects of Hydrogen Bonding on the Photodynamics of Individual Nucleobases in DNA: Comparison of Guanine and Cytosine. *J Am Chem Soc* 2012, *134* (33), 13662–13669
12. Nachtigallová, D.; Barbatti, M.; Szymczak, J. J.; Hobza, P.; Lischka, H. The Photodynamics of 2,4-Diaminopyrimidine in Comparison with 4-Aminopyrimidine: The Effect of Amino-Substitution. *Chem Phys Lett* 2010, *497* (1–3), 129-134
13. Gengeliczki, Z.; Callahan, M. P.; Svadlenak, N.; Pongor, C. I.; Sztáray, B.; Meerts, L.; Nachtigallová, D.; Hobza, P.; Barbatti, M.; Lischka, H.; de Vries, M. S. Effect of Substituents on the Excited-State Dynamics of the Modified DNA Bases 2,4-

Diaminopyrimidine and 2,6-Diaminopurine. *Phys Chem Chem Phys* 2010, *12* (20), 5375–5388

14. Nachtigallová, D.; Hobza, P.; Ritze, H.-H. Electronic Splitting in the Excited States of DNA Base Homodimers and -Trimers: An Evaluation of Short-Range and Coulombic Interactions. *Phys Chem Chem Phys* 2008, *10* (37), 5689-5697
15. Ritze, H.-H.; Hobza, P.; Nachtigallová, D. Electronic Coupling in the Excited Electronic State of Stacked DNA Base Homodimers. *Phys Chem Chem Phys* 2007, *9* (14), 1672-1675
16. Nachtigallová, D.; Aquino, A. J. A.; Horn, S.; Lischka, H. The Effect of Dimerization on the Excited State Behavior of Methylated Xanthine Derivatives: A Computational Study. *Photochem. Photobiol. Sci* 2013, *12* (8), 1498-1508
17. Aquino, A. J. A.; Nachtigallová, D.; Hobza, P.; Truhlar, D. G.; Hattig, C.; Lischka, H. The Charge-Transfer States in a Stacked Nucleobase Dimer Complex: A Benchmark Study. *J. Comput. Chem.* 2010, *32;* 1217-1227
18. Bettanin, F.; Ferrão, L. F. A.; Pinheiro, M.; Aquino, A. J. A.; Lischka, H.; Machado, F. B. C.; Nachtigallova, D. Singlet La and Lb Bands for N-Acenes (N = 2-7): A CASSCF/CASPT2 Study. *J Chem Theory Comput* 2017, *13* (9), 4297–4306
19. Shi, B.; Nachtigallová, D.; Aquino, A. J. A.; Machado, F. B. C.; Lischka, H. High-Level Theoretical Benchmark Investigations of the UV-Vis Absorption Spectra of Paradigmatic Polycyclic Aromatic Hydrocarbons as Models for Graphene Quantum Dots. *J. Chem. Phys* 2019, *150* (12):124302
20. Holá, K.; Sudolská, M.; Kalytchuk, S.; Nachtigallová, D.; Rogach, A. L.; Otyepka, M.; Zbořil, R. Graphitic Nitrogen Triggers Red Fluorescence in Carbon Dots. *ACS Nano* 2017, *11* (12), 12402–12410
21. Langer, M.; Paloncýová, M.; Medveď, M.; Pykal, M.; Nachtigallová, D.; Shi, B.; Aquino, A. J. A.; Lischka, H.; Otyepka, M. Progress and Challenges in Understanding of Photoluminescence Properties of Carbon Dots Based on Theoretical Computations. *Applied Materials Today*. Elsevier Ltd March 1, 2021
22. Shao, X.; Aquino, A. J. A.; Otyepka, M.; Nachtigallová, D.; Lischka, H. Tuning the UV Spectrum of PAHs by Means of Different N-Doping Types Taking Pyrene as Paradigmatic Example: Categorization: Via Valence Bond Theory and High-Level Computational Approaches. *Phys Chem Chem Phys* 2020, *22* (38), 22003–22015
23. Liu, B.; Aquino, A.; Nachtigallova, D.; Lischka, H. Doping Capabilities of Fluorine on the UV Absorption and Emission Spectra of Pyrene-Based Graphene Quantum Dots. *J Phys Chem A 0* (0), null-null. https://doi.org/10.1021/acs.jpca.0c08694
24. Shi, B.; Nachtigallová, D.; Aquino, A. J. A.; Machado, F. B. C.; Lischka, H. Excited States and Excitonic Interactions in Prototypic Polycyclic Aromatic Hydrocarbon Dimers as Models for Graphitic Interactions in Carbon Dots. *Phys Chem Chem Phys* 2019, *21* (18), 9077–9088
25. Shi, B.; Nachtigallová, D.; Aquino, A. J. A.; Machado, F. B. C.; Lischka, H. Emission Energies and Stokes Shifts for Single Polycyclic Aromatic Hydrocarbon Sheets in Comparison to the Effect of Excimer Formation. *J. Phys. Chem Lett* 2019, *10* (18), 5592–5597

CHEMICAL REVIEWS

Review

Cite This: *Chem. Rev.* 2018, 118, 7293−7361

pubs.acs.org/CR

Multireference Approaches for Excited States of Molecules

Hans Lischka,[*,†,‡,§] Dana Nachtigallová,[∥,⊥] Adélia J. A. Aquino,[†,‡,#] Péter G. Szalay,[∇] Felix Plasser,[§,○] Francisco B. C. Machado,[□] and Mario Barbatti[^]

[†] School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin 300072, P.R. China

[‡] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States

[§] Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria

[∥] Institute of Organic Chemistry and Biochemistry v.v.i., The Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

[⊥] Regional Centre of Advanced Technologies and Materials, Palacký University, 78371 Olomouc, Czech Republic

[#] Institute for Soil Research, University of Natural Resources and Life Sciences Vienna, Peter-Jordan-Strasse 82, A-1190 Vienna, Austria

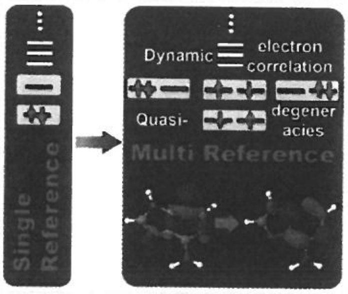
[∇] ELTE Eötvös Loránd University, Laboratory of Theoretical Chemistry, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

[○] Department of Chemistry, Loughborough University, Leicestershire LE11 3TU, United Kingdom

[□] Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos 12228-900, São Paulo, Brazil

[^] Aix Marseille Univ, CNRS, ICR, Marseille, France

ABSTRACT: Understanding the properties of electronically excited states is a challenging task that becomes increasingly important for numerous applications in chemistry, molecular physics, molecular biology, and materials science. A substantial impact is exerted by the fascinating progress in time-resolved spectroscopy, which leads to a strongly growing demand for theoretical methods to describe the characteristic features of excited states accurately. Whereas for electronic ground state problems of stable molecules the quantum chemical methodology is now so well developed that informed nonexperts can use it efficiently, the situation is entirely different concerning the investigation of excited states. This review is devoted to a specific class of approaches, usually denoted as multireference (MR) methods, the generality of which is needed for solving many spectroscopic or photodynamical problems. However, the understanding and proper application of these MR methods is often found to be difficult due to their complexity and their computational cost. The purpose of this review is to provide an overview of the most important facts about the different theoretical approaches available and to present by means of a collection of characteristic examples useful information, which can guide the reader in performing their own applications.



CONTENTS

Special Issue: Theoretical Modeling of Excited State Processes

Received: April 15, 2018
Published: July 24, 2018

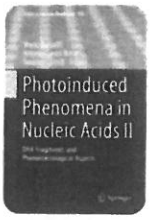
DOI: 10.1021/acs.chemrev.8b00244
Chem. Rev. 2018, 118, 7293−7361

Photoinduced Phenomena in NucleicAcids

Electronic Excitation Processes in Single-Strand and Double-Strand DNA: A Computational Approach

I Chapter I First Online : 01 January 2014

I pp1-37 I



Photoinduced Phenomena in Nucleic Acids Ii

Felix Plasser, **Adélia J.A. Aquino**, **Hans Lischka** & **Dana Nachtigallová**

- **Part of the book series:** Topics in Current Chemistry ((TOPCURRCHEM,volume 356))

Abstract

Absorption of UV light by nucleic acids can lead to damaging photoreactions, which may ultimately lead to mutations of the genetic code. The complexity of the photodynamical behavior of nucleobases in the DNA double-helix provides a great challenge to both experimental and computational chemists studying these processes. Starting from the initially excited states, the main question regards to understanding of the subsequent relaxation processes, which can either utilize monomer-like deactivation pathways or lead to excitonic or charge transfer species with new relaxation dynamics. After a review of photophysical processes in single nucleobases we outline the theoretical background relevant for interacting chromophores and asses a large variety of computational approaches relevant for understanding of the nature and dynamics of excited states of DNA. The discussion continues with the analyses of calculations on excitonic and charge transfer states followed by the presentation of the dynamics of excited-state processes in DNA. The review is concluded by topics o proton transfer in DNA and photochemical dimer formation of nucleobases.

3

Review

Excited state dynamics of DNA bases

Karl Kleinermanns , Dana Nachtigallová & **Mattanjah S. de Vries**

Pages 308-342 | Received 21 Sep 2012, Accepted 18 Dec 2012, Published online: 12 Mar 2013
"Cite this article https://doi.org/10.1080/0144235X.2012.760884

Abstract

Biochemical reactions are subject to the particular environmental conditions of planet earth, including solar irradiation. How DNA responds to radiation is relevant to human health because radiation damage can affect genetic propagation and lead to cancer and is also important for our understanding of how life on earth developed. A reductionist approach to unravelling the detailed photochemistry seeks to establish intrinsic properties of individual DNA building blocks, followed by extrapolation to larger systems, to incorporate interactions between the building blocks and the role of the biomolecular environment. Advances in both experimental and computational techniques have lead to increasingly detailed insights in the excited state dynamics of DNA bases in isolation as well as the role of the solvent and intermolecular interactions. This review seeks to summarise current findings and understanding.

4

PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

The effect of C5 substitution on the photochemistry of uracil

Dana Nachtigallová,*[a] Hans Lischka,*[ab] Jaroslaw J. Szymczak,[b] Mario Barbatti,[b] Pavel Hobza,[a] Zsolt Gengeliczki,[c] Gustavo Pino,[d] Michael P. Callahan[e] and Mattanjah S. de Vries*[f]

Received 7th December 2009, Accepted 2nd March 2010
First published as an Advance Article on the web 27th March 2010
DOI: 10.1039/b925803p

A combined experimental and theoretical study on the excited-state behavior of the uracil analogues, 5-OH-Ura and 5-NH_2-Ura is reported. Two-photon ionization and IR/UV double-resonant spectra show that there is only one tautomer present for each with an excited state lifetime of 1.8 ns for 5-OH-Ura and 12.0 ns for 5-NH_2-Ura as determined from pump–probe experiments. The nature of the excited states of both species is investigated by means of multi-reference *ab initio* methods. Vertical excitation energies, excited state minima, minima on the crossing seam and reaction paths towards them are determined. Sizeable barriers on these paths are found that provide an explanation for the lifetimes of several nanoseconds observed in the experiment.

Introduction

Gas-phase and computational studies of RNA and DNA bases have revealed unique photophysical properties that are sensitive to subtle structural differences. Nucleobase excited-state lifetimes depend on isomerism,[1,2] substitution,[3,4] tautomer form[5,6] and non-covalent interactions, such as hydrogen bonding with complementary bases[7,8] or with solvent molecules[9] and stacking[10] bonding with other nucleobases. Theoretical understanding describes the excited-state dynamics in terms of rapid internal conversion mediated by conical intersections.[8,11–14] This pathway offers a mechanism to diffuse electronic excitation by converting it to ground-state internal energy which can be safely transferred to the environment. One intriguing implication is the possibility that this mechanism could have affected prebiotic chemistry on an early Earth, thus influencing the eventual make-up of the biomolecular building blocks that form life as we know it today.

Conical intersections that couple potential surfaces require geometrical changes in the excited states. For example for 9-methylguanine the internal conversion pathway seems to involve a strongly bent amino group at position 2.[15–17] The pathway for cytosine appears to involve C=C twisting[18,19] with a low barrier for keto-cytosine (producing a short vibronic spectrum[20]) and a considerable energy gap to the S_0 state for enol-cytosine, producing an extensive vibronic spectrum.[20] Therefore it should be no surprise that the potential energy landscapes that form conical intersections are affected by different substitutions. Excited-state dynamics should be especially sensitive to substitutions in the positions of the molecular frame that include coordinates along which the intersections are formed.

Among several works dealing with the effect of substitution in photoexcited nucleobases[4,14,21–28] we would like to draw attention to the recent work by Mburu and Matsika.[4] These authors have explored the effect of substitutions on purines and found that substitution at the C2 position decreases the energy of the first $\pi\pi^*$ state considerably whereas substitution at the C6 position has a much smaller effect; the carbonyl group has in general a stronger effect than the amino group; $n\pi^*$ states for all substituted purines are blue-shifted compared to purine. To understand the effect on pyrimidine bases they compared with 2-pyrimidinone (the ring structure of cytosine without the amino group) and found that the energy of the first bright excited state correlates strongly with the nature, position, and orientation of the substituent.

We have also recently explored the effect of amino substitutions in pyrimidines by studying 2,4-diaminopyrimidine by means of multi-reference *ab initio* methods.[29] The calculations of stationary points in the ground and excited states, minima on the S_0/S_1 crossing seam and connecting reaction paths show that several paths with negligible barriers exist, allowing ultrafast radiationless deactivation if excited at energies slightly higher than the band origin. Even though the NH_2 group attached to the C2 position blocks the path to one of the lowest energy conical intersections, namely the one associated with ring puckering at C2, there are still other alternatives for almost barrierless access to conical intersections associated with deformations at the C5, C6, and N1 positions.

Substituted uracil compounds can be viewed as structural analogues of 2,4-diaminopyrimidine in which the C2 and C4 positions are substituted by oxygen rather than amino groups (see Fig. 1). We now report the effect of substitution at the C5

---

[a] *Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic. E-mail: dana.nachtigallova@uochb.cas.cz, hans.lischka@univie.ac.at*
[b] *Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A1090 Vienna, Austria*
[c] *Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA*
[d] *National University of Cordoba, Argentina*
[e] *NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA*
[f] *Department of Chemistry and Biochemistry, University of California Santa Barbara, CA-93106-9510, USA. E-mail: devries@chem.ucsb.edu; Fax: (+1) 805-893-4120; Tel: (+1) 805-893-5921*

Relaxation mechanisms of UV-photoexcited DNA and RNA nucleobases

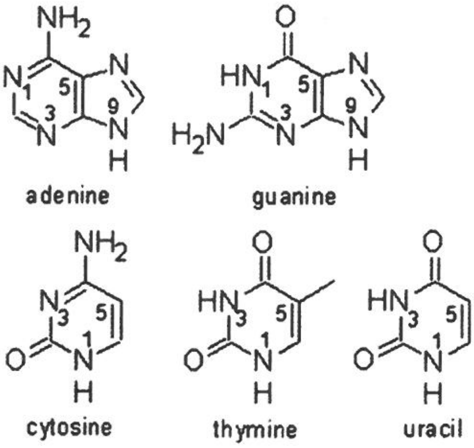
Mario Barbatti[a,b,1], **Adélia J. A. Aquino**[a], **Jaroslaw J. Szymczak**[a], **Dana Nachtigallová**[c], **Pavel Hobza**[c], **and Hans Lischka**[a,c,1]

[a]Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A 1090 Vienna, Austria; [b]Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D 45470 Mülheim an der Ruhr, Germany; and [c]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic.

Edited* by Josef Michl, University of Colorado at Boulder, Boulder, CO, and approved October 15, 2010 (received for review October 6, 2010)

A comprehensive effort in photodynamical ab initio simulations of the ultrafast deactivation pathways for all five nucleobases adenine, guanine, cytosine, thymine, and uracil is reported. These simulations are based on a complete nonadiabatic surface-hopping approach using extended multiconfigurational wave functions. Even though all five nucleobases share the basic internal conversion mechanisms, the calculations show a distinct grouping into purine and pyrimidine bases as concerns the complexity of the photodynamics. The purine bases adenine and guanine represent the most simple photodeactivation mechanism with the dynamics leading along a diabatic $\pi\pi^*$ path directly and without barrier to the conical intersection seam with the ground state. In the case of the pyrimidine bases, the dynamics starts off in much flatter regions of the $\pi\pi^*$ energy surface due to coupling of several states. This fact prohibits a clear formation of a single reaction path. Thus, the photodynamics of the pyrimidine bases is much richer and includes also $n\pi^*$ states with varying importance, depending on the actual nucleobase considered. Trapping in local minima may occur and, therefore, the deactivation time to the ground state is also much longer in these cases. Implications of these findings are discussed (*i*) for identifying structural possibilities where singlet/triplet transitions can occur because of sufficient retention time during the singlet dynamics and (*ii*) concerning the flexibility of finding other deactivation pathways in substituted pyrimidines serving as candidates for alternative nucleobases.

photodynamical simulation | photostability | ultrafast photodeactivation | nonadiabatic interactions | ab initio multireference methods



Scheme 1.

Owing to the importance of mutagenic and carcinogenic effects caused by UV radiation on DNA, the UV-induced photochemistry and photophysics of individual bases (1–7), base pairs (8–10), and nuclei acid strands (11–13) have been intensively studied. In each of these levels, it has been found that the genetic code may count on molecular mechanisms to get rid of the energy excess minimizing deleterious effects. Isolated nucleobases (Scheme 1), for instance, are all photostable by returning to the ground state in an ultrafast time scale of a few picoseconds (1, 2, 14–20), which reduces the probability of undergoing photochemical transformations induced by reactive excited states. The ultrafast deactivation of the five natural nucleobases contrasts with the long lifetime of analogous bases not found in DNA and RNA (2, 21), suggesting that it could have been a source of evolutionary pressure in early biotic ages.

Ultrafast deactivation occurs through internal conversion mechanisms, where the molecule transfers the photoenergy stored in the electronic system to nuclear vibrational degrees of freedom. This means, the deactivation takes place without photoemission in contrast to what occurs for fluorescent and phosphorescent species. The energy transfer proceeds more intensely near nuclear geometries with state degeneracies also known as conical intersections, which motivates the search for mechanisms explaining how the molecular geometry is deformed from the ground state (or Franck–Condon) structure initially photoexcited into the strongly distorted geometries where conical intersections usually occur.

Even though the nucleobases share the property of photostability, their structures, electronic properties, and spectra show considerable variation. Therefore, the question arises whether there is a common pattern in the deactivation dynamics of the nucleobases or does one encounter only a collection of processes that finally lead to the same result of photostability. Advanced techniques of theoretical chemistry are very well suited for performing such comparative studies even though the severe difficulties have to be recognized where several electronic states and their nonadiabatic interactions have to be considered at the same time. Together with ultrafast time-resolved spectroscopy (1, 2, 22), these methods have provided a high degree of detail in the characterization of internal conversion processes, suggesting ring puckering as one major structural theme for the photodeactivation of nucleobases (3, 23–26). Based on the available knowledge of computed structures and connecting reaction paths, a unifying description of the photostability of all nucleobases has been proposed (5, 23, 27). However, considering the fact that up to now for all nucleobases about 20 energetically accessible minimum energy conical intersection structures, which still describe the intersection seam only in a rudimentary way, are known, the goal of providing a theoretical explanation for the photodynamics based on description of reaction paths alone seems to be almost

---

Author contributions: H.L. designed research; M.B., A.J.A.A., J.J.S., D.N., and H.L. performed research; M.B., A.J.A.A., J.J.S., D.N., P.H., and H.L. analyzed data; and M.B., A.J.A.A., J.J.S., D.N., P.H., and H.L. wrote the paper.

The authors declare no conflict of interest.

*This Direct Submission article had a prearranged editor.

[1] To whom correspondence may be addressed. E-mail: barbatti@kofo.mpg.de or hans.lischka@univie.ac.at.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1014982107/-/DCSupplemental.

12686 J. Phys. Chem. A 2009, 113, 12686–12693

6

Photodynamics Simulations of Thymine: Relaxation into the First Excited Singlet State[†]

Jaroslaw J. Szymczak,[*,‡] **Mario Barbatti,**[*,‡] **Jason T. Soo Hoo,**[§] **Jaclyn A. Adkins,**[‖]
Theresa L. Windus,[⊥] **Dana Nachtigallová,**[#] **and Hans Lischka**[*,‡,#]

Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A 1090 Vienna, Austria, Departments of Physics, Siena College, 515 Loudon Road, Loudonville, New York 12211, Department of Chemistry, Northwest Missouri State University, 800 University Drive, Maryville, Missouri 64468, Department of Chemistry, Iowa State University, 1605 Gilman Hall, Ames, Iowa 50011, and Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic

Received: May 30, 2009; Revised Manuscript Received: August 1, 2009

Ab initio nonadiabatic dynamics simulations are reported for thymine with focus on the $S_2 \rightarrow S_1$ deactivation using the state-averaged CASSCF method. Supporting calculations have been performed on vertical excitations, S_1 and S_2 minima, and minima on the crossing seam using the MS-CASPT2, RI-CC2, MR-CIS, and MR-CISD methods. The photodynamical process starts with a fast (<100 fs) planar relaxation from the S_2 $\pi\pi^*$ state into the $\pi_O\pi^*$ minimum of the S_2 state. The calculations demonstrate that two π-excited states (denoted $\pi\pi^*$ and $\pi_O\pi^*$) are actually involved in this stage. The time in reaching the S_2/S_1 intersections, through which thymine can deactivate to S_1, is delayed by both the change in character between the states as well as the flatness of the S_2 surface. This deactivation occurs in an average time of 2.6 ps at the lowest-energy region of the crossing seam. After that, thymine relaxes to the $n\pi^*$ minimum of the S_1 state, where it remains until the transfer to the ground state takes place. The present dynamics simulations show that not only the $\pi_O\pi^*$ S_2 trapping but also the trapping in the $n\pi^*$ S_1 minimum contribute to the elongation of the excited-state lifetime of thymine.

1. Introduction

Upon UV excitation, all five naturally occurring nucleobases return to the ground state on an ultrafast time scale ranging from half a picosecond to a few picoseconds.[1–5] The ultrafast decay minimizes the time that the molecule remains in reactive excited states, which could induce photochemical damage. This enhanced photostability might have been one factor favoring the selection of these bases in early biotic ages, to the detriment of other similar molecules with long-lived excited states.

In general, ultrafast decay depends on the existence of reaction pathways connecting the Franck–Condon region to the seam of conical intersections between the excited and ground states where radiationless processes can occur. For this reason, a great deal of theoretical work has been dedicated to the characterization of reaction paths and conical intersections not only for the five nucleobases[6–18] but also for their isomers,[11,19] substituted species,[12,20,21] and base models.[22,23] Further progress has been achieved by means of dynamics simulations, which attempt to describe the excited-state time evolution and the most frequently accessed reaction pathways. However, balancing the computational costs of dynamics simulations lasting for several picoseconds while still maintaining a proper description of multiple electronic excited states and their nonadiabatic couplings still constitutes a major challenge. Despite the difficulties, semiempirical,[24–26] density functional,[27] and ab initio[28–31] nonadiabatic dynamics simulations have been reported recently for nucleobases.

Among the five nucleobases, thymine has the longest lifetime.[1,2] Femtosecond-resolved pump–probe resonant ionization experiments pumped at 267 nm have revealed two exponential decay components, 6.4 and 100 ps, with the longer one assigned to the triplet-state population.[2] Another set of mass-selected femtosecond-resolved pump–probe resonant ionization experiments also pumped at 267 nm and identified a two-step mechanism with time constants 105 fs and 5.12 ps.[1] In the time-resolved photoelectron spectroscopy experiments reported in ref 4, three time constants were obtained, <50, 490 and 6.4 ps (pump energy at 250 nm). Even though there is no full agreement about the details of the deactivation process, a time constant in the range of 5 to 6 ps for deactivation to the ground state clearly emerges from all of these experimental results. This time constant is, in addition, much larger than those measured for the other nucleobases (adenine: 1.1 ps, cytosine: 1.86 ps, guanine: 0.36 ps, uracil: 1.05 ps[1]).

On the basis of the reaction paths connecting the Franck–Condon region to the S_1/S_0 conical intersections, Perun et al.[13] have proposed that the relatively long lifetime of thymine could be explained by a trapping of the molecule in the dark S_1 $n\pi^*$ state after fast deactivation from the S_2 $\pi\pi^*$ state. Nevertheless, multiple spawning dynamics simulations performed by Hudock et al.[29] at the complete active space self-consistent field (CASSCF) level have found a surprisingly small $S_2 \rightarrow S_1$ deactivation yield in the first half picosecond. These authors then proposed that the reason for the long lifetime is the trapping of thymine in a S_2 minimum right after the photoexcitation. On the basis of the analysis of the reaction paths connecting the minimum in the S_1 state to the S_1/S_0 conical intersections, Zechmann and Barbatti[14] have discussed how the low efficiency of those paths should be an additional factor adding to the S_2 trapping to delay the deactivation to the ground state. Recently

---

[†] Part of the "Russell M. Pitzer Festschrift".

[*] Corresponding authors. E-mail: jaroslaw.szymczak@univie.ac.at (J.J.S.); mario.barbatti@univie.ac.at (M.B.); hans.lischka@univie.ac.at (H.L.).

[‡] University of Vienna.

[§] Siena College.

[‖] Northwest Missouri State University.

[⊥] Iowa State University.

[#] Academy of Sciences of the Czech Republic.

10.1021/jp905085x CCC: $40.75

THE JOURNAL OF
PHYSICAL CHEMISTRY

ARTICLE

pubs.acs.org/JPCA

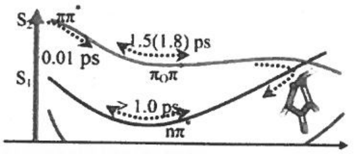
Nonadiabatic Dynamics of Uracil: Population Split among Different Decay Mechanisms

Dana Nachtigallová,[*,†] Adélia J. A. Aquino,[‡] Jaroslaw J. Szymczak,[‡,⊥] Mario Barbatti,[*,§] Pavel Hobza,[†] and Hans Lischka[*,‡]

[†]Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic
[‡]Institute of Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A 1090 Vienna, Austria
[§]Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim, Germany

Ⓢ *Supporting Information*

ABSTRACT: Nonadiabatic dynamics simulations performed at the state-averaged CASSCF method are reported for uracil. Supporting calculations on stationary points and minima on the crossing seams have been performed at the MR-CISD and CASPT2 levels. The dominant mechanism is characterized by relaxation into the S_2 minimum of $\pi\pi^*$ character followed by the relaxation to the S_1 minimum of $n\pi^*$ character. This mechanism contributes to the slower relaxation with a decay constant larger than 1.5 ps, in good agreement with the long time constants experimentally observed. A minor fraction of trajectories decay to the ground state with a time constant of about 0.7 ps, which should be compared to the experimentally observed short constant. The major part of trajectories decaying with this time constant follows the $\pi\pi^*$ channel and hops to the ground state via an ethylenic conical intersection. A contribution of the relaxation proceeding via a ring-opening conical intersection was also observed. The existence of these two latter channels together with a reduced long time constant is responsible for a significantly shorter lifetime of uracil compared to that of thymine.



1. INTRODUCTION

Upon UV excitation all five naturally occurring nucleobases relax into the ground state through internal conversion mechanisms on time scales not exceeding a few picoseconds,[1−6] in contrast to some of their analogues not found in nucleic acids.[1,7] This ultrafast decay serves as a protection mechanism, which prevents photochemical damage. This remarkable photostability of the nucleobases has been investigated intensively by means of experimental and theoretical approaches.

Ultrafast pump−probe techniques[1−4,6−8] have been applied in order to obtain detailed information on the specific time scales of the deactivation processes. For the purine bases, adenine and guanine,[1,2,4,6,8,9] experimental data indicate a single homogeneous mechanism with a faster decay compared to pyrimidine bases. The experimental studies performed on the pyrimidine bases, thymine, uracil, and cytosine, reveal more complicated photodynamics with generally longer lifetimes; the longest one is for thymine.[1,2,4] For uracil, using gas phase time-resolved photoelectron spectra obtained with a pump wavelength of 250 nm, three time constants were determined: a decay of less than 0.05 ps, followed by intermediary (0.53 ps) and longer (2.4 ps) decay constants.[4] Using the same initial energy, mass-selected femtosecond-resolved pump−probe ionization measurements were fitted with two exponentials, giving short and long decay times of 0.13 and 1.05 ps, respectively.[1] Kang et al. used a monoexponential fit in the analysis of femtosecond-resolved pump−probe resonant ionization spectra with 267 nm pump wavelength. They reported an exponential decay of 2.4 ps.[2] All these experimental results agree on a faster decay than that of thymine,[1,2,4] for which lifetimes of 6.4 and 5.1 ps have been obtained. A dark state with a lifetime of several nanoseconds found in time-resolved photoelectron spectra of uracil and thymine was explained by trapping in the $n\pi^*$ state.[10,11]

Many theoretical studies have been performed to obtain a molecular picture explaining the observed ultrafast decay mechanisms. Reaction paths and conical intersections between energy surfaces of different electronic states have been computed for the natural nucleobases,[12−24] nucleobase models,[25−27] isomers,[17,28] and substituted species.[7,20,23,26] Special emphasis must be attributed to these conical intersections and their energetic accessibility since they are responsible for the ultrafast nonradiative decay occurring in the nucleobases.

Concentrating the discussion on uracil, the energetically lowest conical intersection found so far on the S_2/S_1 crossing seam has a boat conformation.[19,29,30] Two main conical intersections for $S_1 \rightarrow S_0$ deactivation were identified for uracil. The first one is an ethylenic conical intersection formed by twisting of the C_5-C_6 bond, which promotes a crossing between the $\pi\pi^*$ and closed shell (cs) states. The second conical intersection, found by Lan et al. using the semiempirical OM2 approach, is formed by out-of-plane distortion of the oxygen atom connected to the C_4 atom, causing a crossing between the $n\pi^*$ and the closed shell states.[31] On the basis of these investigations, different mechanisms have been proposed to explain the photophysical deactivation to the

Received: February 10, 2011
Revised: April 15, 2011
Published: May 06, 2011

dx.doi.org/10.1021/jp201327w | *J. Phys. Chem. A* 2011, 115, 5247–5255

THE JOURNAL OF CHEMICAL PHYSICS **134**, 014304 (2011)

The decay mechanism of photoexcited guanine – A nonadiabatic dynamics study

Mario Barbatti,[1,2,a)] Jaroslaw J. Szymczak,[2,b)] Adélia J. A. Aquino,[2] Dana Nachtigallová,[3] and Hans Lischka[2,c)]
[1]*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany*
[2]*Institute for Theoretical Chemistry - University of Vienna, Waehringerstrasse 17, A 1090 Vienna, Austria*
[3]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic*

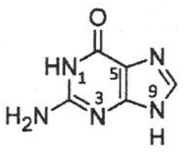
(Received 8 October 2010; accepted 8 November 2010; published online 7 January 2011)

Ab initio surface hopping dynamics calculations were performed for the biologically relevant tautomer of guanine in gas phase excited into the first $\pi\pi^*$ state. The results show that the complete population of UV-excited molecules returns to the ground state following an exponential decay within ~220 fs. This value is in good agreement with the experimentally obtained decay times of 148 and 360 fs. No fraction of the population remains trapped in the excited states. The internal conversion occurs in the $\pi\pi^*$ state at two related types of conical intersections strongly puckered at the C2 atom. Only a small population of about 5% following an alternative pathway via a $n\pi^*$ state was found in the dynamics. © *2011 American Institute of Physics*. [doi:10.1063/1.3521498]

I. INTRODUCTION

Like the four other natural nucleobases, UV-excited guanine shows ultrafast radiationless deactivation in gas phase with a decay time of a few picoseconds in the maximum,[1–3] which implies that it returns to the ground state by means of an internal conversion mechanism. These ultrafast deactivation mechanisms of guanine and of the other nucleobases and their related photostability are of great interest since they are considered to contribute to a natural chemical defense of the genetic code against damaging photochemically induced processes in reactive excited states.[4]

The guanine deactivation processes have been measured at 267 nm pump wavelength,[1–3] slightly below the center of the first absorption band (284 nm).[5] The exact time constants depend on the details of the experimental setup and on the way of the transient spectra are analyzed. When only the non-fragmented guanine channel is included in the analysis of the transient spectrum, guanine deactivation has been explained by two time constants of 0.148 and 0.36 ps.[2] When, however, fragment mass channels are included as well, the longer time constant has been found to increase more than six times to 2.3 ps.[3]



SCHEME 1.

Three main reaction pathways have been identified computationally for internal conversion of guanine (9H-1H-keto-guanine, Scheme 1) from the first $\pi\pi^*$ state to the ground state. The first one is a barrierless pathway with the electronic state characterized as $\pi\pi^*$ excitation and the nuclear motion described by puckering of the C2 atom and displacement of the amino group out of the ring plane.[6–10] Two slightly different kinds of conical intersections (denoted *ethylenic I* and *ethylenic II*) can be accessed through this pathway. The second pathway leads to a conical intersection characterized by puckering of the C6 atom and displacement of the oxygen atom out of the ring plane.[6–8] The third alternative is characterized by stretching of one of the NH bonds, promoting an intersection of the $\pi\sigma^*$ state with the ground state. Reference 9 shows that this pathway may contribute to the deactivation for excitation energies around 0.4 eV above the absorption maximum of the first bright $\pi\pi^*$ state. In the present, work we concentrated on a narrower range of excitation energies below values relevant to N-H dissociation and, therefore, did not consider this reaction channel further.

The guanine decay dynamics (see Ref. 2 and discussion above) has been interpreted by Serrano-Andrés *et al.*[7] by a three-state model based on computed minimum energy paths. The fast decay time observed experimentally (0.148 fs) has been assigned to a direct decay path to the first type of conical intersection (*ethylenic II*), whereas for the explanation of the longer decay time (360 fs) another alternative passing through the S_1 $n\pi^*$ minimum has been suggested. Such specific assignments based on static calculations alone are difficult. Dynamics simulations are certainly the appropriate tool to resolve such mechanistic alternatives directly.

So far, non-adiabatic dynamics simulations for excited guanine have been performed with potential energy surfaces computed only with restricted open-shell Kohn–Sham (ROKS)[11] and semi-empirical OM2/MRCI[8] methods, predicting strongly differing results. The ROKS simulations for 9-methyl-guanine and 7-methyl-guanine do not show the involvement of conical intersections. Instead, the internal

---

[a)] Electronic mail: barbatti@mpi-muelheim.mpg.de.
[b)] Electronic mail: jaroslaw.szymczak@univie.ac.at.
[c)] Electronic mail: hans.lischka@univie.ac.at.

0021-9606/2011/134(1)/014304/5/$30.00

PHOTODYNAMICS OF THE ADENINE MODEL 4-AMINOPYRIMIDINE EMBEDDED WITHIN DOUBLE STRAND OF DNA

Tomáš ZELENÝ[a], Pavel HOBZA[b1], Dana NACHTIGALLOVÁ[b2,*],
Matthias RUCKENBAUER[c1] and Hans LISCHKA[c2,*]

[a] *Department of Physical Chemistry, Faculty of Sciences, Palacký University, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic; e-mail: tomas.zeleny@upol.cz*

[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2, 166 10 Prague 6, Czech Republic; e-mail: [1] pavel.hobza@uochb.cas.cz, [2] dana.nachtigallova@uochb.cas.cz*

[c] *Institute of Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A 1090 Vienna, Austria; e-mail: [1] matthias.ruckenbauer@univie.ac.at, [2] hans.lischka@univie.ac.at*

Received February 23, 2011
Accepted April 12, 2011

Dedicated to Dr. Zdeněk Havlas on the occasion of his 60th birthday.

On-the-fly surface hopping nonadiabatic photodynamical simulations using hybrid quantum mechanical/molecular mechanical approach of 4-aminopyrimidine were performed to model the relaxation mechanism of adenine within DNA double strand. The surrounding bases do not affect the overall ring-puckering relaxation mechanisms significantly, however, interesting hydrogen-bond dynamics is observed. First, formation of intra-strand hydrogen bonds is found. It is shown that this effect speeds up the decay process. In addition, the Watson–Crick structure is altered by breaking one of the inter-strand hydrogen bonds also leading to a decrease of the life time.

Keywords: *Ab initio* calculations; Excited states; Nucleic acids; Photodynamics; QM/MM method.

The nature of the excited states of DNA/RNA nucleic acids induced by UV radiation has been studied extensively over the last decades. To understand the photochemistry of these compounds, the excited state behavior of individual bases[1–19], base pairs[20–24] and nucleic acid strands[25–31] has been studied both experimentally and theoretically. The ultrafast relaxation of excited states of isolated species, on the time scale of a few picoseconds has been the subject of several computational studies performed by means of nonadiabatic dynamics simulations[11–15,32,33]. It is now generally accepted that nucleobases relax into the ground state through nonadiabatic transi-

Collect. Czech. Chem. Commun. 2011, Vol. 76, No. 6, pp. 631–643

doi:10.1135/cccc2011046

J|A|C|S
COMMUNICATIONS

Does Stacking Restrain the Photodynamics of Individual Nucleobases?

Dana Nachtigallová,[*,†] Tomáš Zelený,[†,‡] Matthias Ruckenbauer,[§] Thomas Müller,[‖] Mario Barbatti,[§,⊥] Pavel Hobza,[†,‡] and Hans Lischka[*,†,§]

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 166 10 Praha 6, Czech Republic, Department of Physical Chemistry, Faculty of Science, Palacký University, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic, Institute of Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A 1090 Vienna, Austria, and Institute of Advanced Simulation, Jülich Supercomputer Centre, Research Centre Jülich, D-52425 Jülich, Germany

Received April 8, 2010; E-mail: dana.nachtigallova@uochb.cas.cz; hans.lischka@univie.ac.at

Nonadiabatic photodynamical simulations of 4-aminopyrimidine (4-APy) used as a model for adenine were performed by embedding it between two stacking methyl-guanine (mGua) molecules to determine the effect of spatial restrictions on the ultrafast photodeactivation mechanism of this nucleobase. During the dynamics the formation of a significant fraction of intrastrand hydrogen bonding from 4-APy to mGua above and below is observed. These findings show that this type of hydrogen bond may play an important role for the photodynamics within one DNA strand and that it should be of interest even in irregular segments of double stranded nucleic acids structures. The relaxation mechanism of internal conversion to the ground state is dominated by ring puckering, and an overall elongation of the lifetime by ~20% as compared to the isolated 4-APy is computed.

Ultrafast relaxation of excited states of naturally occurring nucleobases on the time scale of a few picoseconds is a well-known phenomenon.[1-4] Computational studies performed by means of static[5-8] and nonadiabatic dynamics simulations[9-12] helped to reveal the excited-state time evolution of nucleobases as isolated species. It is generally accepted that isolated nucleobases relax into the ground state through nonadiabatic transitions via conical intersections characterized by strongly ring-puckered structures. Experimental observations[13-15] supported by theoretical calculations[16-18] indicate that in DNA excimers and/or excitons can be formed affecting the resulting excited-state lifetime strongly. Additionally, localization of the excitation on a single base, which is expected to resemble the behavior of the isolated base, has been reported as well.[14]

The theoretical treatment of the photodynamics of DNA, especially explicit nonadiabatic simulations, is quite involved, and corresponding investigations are only at the beginning.[19-21] In this contribution we focus in a first step on steric effects which adjoining nucleobases will have on an embedded base and its possibilities to reach conical intersections. These calculations are performed in the framework of on-the-fly surface hopping dynamics simulations which provide a detailed picture of the occurring photophysical processes. A combined quantum mechanical/molecular mechanical (QM/MM)[22-24] approach is used in which 4-APy is embedded between two methyl-guanine molecules (see Figure 1). The methyl groups were used to terminate the N-glycosidic bond in Gua. In these calculations the electronic excitation is confined to 4-APy, which is treated quantum mechanically, whereas the mGua molecules are treated at the MM level. Although this approach does not account for the electronic reactivity of 4-APy with adjacent nucleobases, it provides information on their possible sterical constraints during the excited state decay. Based on previous experience with dynamics simulations on isolated 4-APy[25-27] this molecule has been chosen because it is flexible enough to allow investigating restrictions to puckering at C_2 and C_4 atoms, relevant for purine bases, and at the C_6 atom, relevant for pyrimidine bases (for numbering scheme, see Figure 2).

The stacking model of mGua−4-APy−mGua was obtained by replacing adenine with 4-APy in the Gua−Ade−Gua sequence cut out from a B-DNA dodecamer crystal structure (PDBID: 196D).[28] These results are compared to those obtained from photodynamics simulation of isolated 4-APy[27] performed with identical procedures for creating initial conditions as used in the present study.

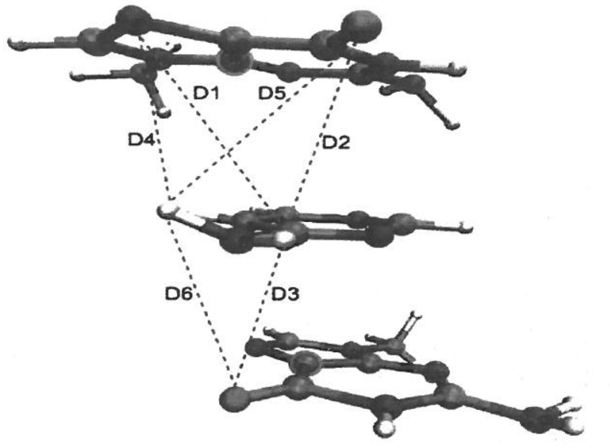


Figure 1. Starting structure of mGua−4-APy−mGua for dynamics calculations. Distances D1−D6 were used to analyze possible hydrogen bonds forming through the dynamics simulation. The atoms constrained by harmonic potential function are highlighted by red circles.

The 4-APy (QM part) was calculated at the state-averaged complete active space self-consistent field (SA-CASSCF) level of theory. A state averaging procedure with three states (SA-3) was used throughout the calculations. The active space was composed of two lone pair orbitals localized on nitrogen atoms of the pyrimidine ring and three π orbitals and three π^* orbitals, i.e., 10 electrons in 8 orbitals (CAS(10,8)). The molecular orbitals were expanded in the 6-31G* basis set.[29,30] Analytic energy gradients and nonadiabatic coupling vectors required for the dynamics were computed as described in refs 31−34 using the COLUMBUS program system.[35-37]

[†] Academy of Sciences of the Czech Republic.
[‡] Palacký University.
[§] University of Vienna.
[‖] Research Centre Jülich.
[⊥] Present address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim, Germany.

10.1021/ja1029705

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Strikingly Different Effects of Hydrogen Bonding on the Photodynamics of Individual Nucleobases in DNA: Comparison of Guanine and Cytosine

Tomáš Zelený,[†] Matthias Ruckenbauer,[‡,#] Adelia J.A. Aquino,[‡,§,||] Thomas Müller,[⊥] Filip Lankaš,[⊗] Tomáš Dršata,[⊗] William L. Hase,[§] Dana Nachtigallova,[*,⊗] and Hans Lischka[*,‡,§]

[†] Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University Olomouc, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic

[‡] Institute of Theoretical Chemistry, University of Vienna, Währingerstraße 17, A-1090 Vienna, Austria

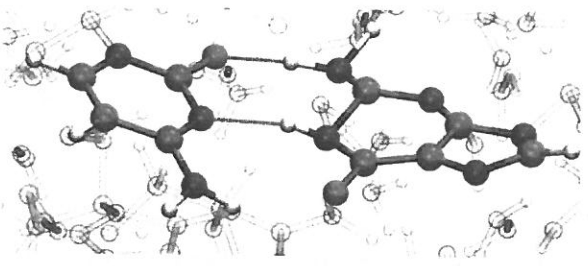
[§] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States

[||] Institute of Soil Research, University of Natural Resources and Life Sciences, Peter-Jordan-Straße 82, A-1190 Vienna, Austria

[⊥] Institute of Advanced Simulation, Jülich Supercomuter Centre, Forschungszentrum Jülich, D-52425 Jülich, Germany

[⊗] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 166 10 Prague, Czech Republic

Supporting Information



ABSTRACT: Ab initio surface hopping dynamics calculations were performed to study the photophysical behavior of cytosine and guanine embedded in DNA using a quantum mechanical/molecular mechanics (QM/MM) approach. It was found that the decay rates of photo excited cytosine and guanine were affected in a completely different way by the hydrogen bonding to the DNA environment. In case of cytosine, the geometrical restrictions exerted by the hydrogen bonds did not influence the relaxation time of cytosine significantly due to the generally small cytosine ring puckering required to access the crossing region between excited and ground state. On the contrary, the presence of hydrogen bonds significantly altered the photodynamics of guanine. The analysis of the dynamics indicates that the major contribution to the lifetime changes comes from the interstrand hydrogen bonds. These bonds considerably restricted the out-of-plane motions of the NH_2 group of guanine which are necessary for the ultrafast decay to the ground state. As a result, only a negligible amount of trajectories decayed into the ground state for guanine embedded in DNA within the simulation time of 0.5 ps, while for comparison, the isolated guanine relaxed to the ground state with a lifetime of about 0.22 ps. These examples show that, in addition to phenomena related to electronic interactions between nucleobases, there also exist relatively simple mechanisms in DNA by which the lifetime of a nucleobase is significantly enhanced as compared to the gas phase.

INTRODUCTION

In the last decades, impressive progress has been achieved in the understanding of the photodynamics of nucleic acids. The experimentally observed ultrafast excited state relaxation of all five naturally occurring nucleobases[1−6] has been explained by internal conversion via conical intersections.[7−18] The excited state behavior of nucleobases embedded within the DNA or RNA structure is, however, much less understood. The complex behavior of their excited state decay made it difficult to resolve the relaxation mechanisms in molecular detail. It has been shown in several experimental studies that the decay properties of nucleic acids in DNA depend on the base sequence and the conformation.[4,19−28] In contrast to isolated nucleic acid bases in gas phase and water, where conversion to the ground state occurs on picosecond or subpicosecond time scale, the relaxation of nucleobases in DNA ranges in the picosecond and up to hundreds of picoseconds time scale. On the basis of the experimental observations, it has been suggested that in addition to excited states localized on single nucleobases also delocalized exciton and excimer/exciplex complexes are responsible for nonradiative relaxation of nucleic acids.[19,21,23,29−38] Static quantum chemical calculations which can provide information about the character of excimer/exciplex complexes and the influence of both, inter- and intrastrand interactions within the DNA helix[39−48] support these suggestions. The relaxation mediated by a proton-transfer within base-pairs was suggested also.[49] The role of the second strand, and consequently this type of relaxation mechanism, was, however, lately questioned by Crespo-Hernandez et al.[19]

Received: March 24, 2012
Published: July 30, 2012

dx.doi.org/10.1021/ja3028845 | J. Am. Chem. Soc. 2012, 134, 13662−13669

Chemical Physics Letters 497 (2010) 129–134

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

The photodynamics of 2,4-diaminopyrimidine in comparison with 4-aminopyrimidine: The effect of amino-substitution

Dana Nachtigallová [a,*], Mario Barbatti [b,**], Jaroslaw J. Szymczak [c], Pavel Hobza [a], Hans Lischka [a,c,***]

[a] *Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic*
[b] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim, Germany*
[c] *Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A1090 Vienna, Austria*

ARTICLE INFO

Article history:
Received 9 April 2010
In final form 29 July 2010
Available online 5 August 2010

ABSTRACT

Nonadiabatic photodynamical surface hopping simulations of 4-aminopyrimidine and 2,4-diaminopyrimidine were performed at multi-configurational level. Additional NH_2 substitution blocks part of the ring puckering modes necessary to reach ultrafast deactivation channels but does not affect the excited-state lifetime of 2,4-diaminopyrimidine significantly since other pathways leading to ultrafast relaxation can be utilized.

The effect of the excess energy on the relaxation mechanism of 2,4-diaminopyrimidine was studied. It is shown that the amount of initial energy influences the time to reach the crossing seam and thus the lifetime. This study is important when interpreting the experimental results performed at different pump energies.

1. Introduction

The nature of the excited state of DNA and RNA bases have been recently studied both experimentally and theoretically by several groups. In the gas phase the five naturally occurring nucleic acid bases have an ultrafast relaxation of the excited state to the ground state [1–6] which is explained by a rapid internal conversion via conical intersections [7–19].

Structural differences are known to modify the excited-state lifetime of these species and their related compounds. Long lived excited states of other tautomeric forms than naturally occurring nucleic acid bases have been reported [7,20]. The substitution of certain parts of the ring might affect the excited states lifetimes by blocking these parts and making relevant conical intersections inaccessible. A well known example is 2-aminopurine whose amino group at the C2 position leads to a much longer excited-state lifetime than of adenine (6-aminopurine) [21,22].

Study of the photophysics and photochemistry of model compounds with substitutions at the different position of the rings is especially important for the understanding of the nature of their ultrafast deactivation through specific conical intersection. One of the main theoretical tools in these investigations is the nonadiabatic dynamics simulation which can provide information about the main relaxation pathways and the time scales of the relaxation process.

Recently, we have performed a combined experimental and theoretical study on the modified DNA base 2,4-diaminopyrimidine (2,4-DAPy; see **Scheme 1**) [23].

The static quantum chemical calculations clearly show that conical intersections are accessible when this molecule is excited near the absorption band maximum and, thus, an ultrafast (few ps) radiationless decay was predicted. In the experiments performed in the just-mentioned work pump energies near to the band origin were used revealing a much longer (estimated in the time range of 10 ps–1 ns) excited-state lifetime than what would be expected for a radiationless decay. This situation implies that sufficient energy must be available to overcome barriers before entering into the internal conversion regime and the photodynamics should be sensitive in this case to the pump energy used.

It was the goal of this work to study the photophysics of 2,4-DAPy by means of dynamics simulations in order to obtain explicit information on reaction mechanisms and lifetimes. The first objective was the evaluation of the overall influence of substituents on the relaxation mechanism of the pyrimidine ring by comparing 2,4-DAPy with 4-APy. The additional NH_2 substitution at the C2 atom can block specific decay channels and, consequently, increase the excited-state lifetime of 2,4-DAPy compared to 4-APy. The second aspect of this investigation concerns the afore-mentioned effect of the excess energy on the character of the dynamics by monitoring the dynamics simulations in dependence of different excitation energies. With higher energies a larger variety of conical intersections located on different crossing seams

---

* Corresponding author.
** Corresponding author.
*** Corresponding author at: Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic.
E-mail address: dana.nachtigallova@uochb.cas.cz (D. Nachtigallová).

0009-2614/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2010.07.098

Effect of substituents on the excited-state dynamics of the modified DNA bases 2,4-diaminopyrimidine and 2,6-diaminopurine†

Zsolt Gengeliczki,[a] Michael P. Callahan,[c] Nathan Svadlenak,[c]
Csaba István Pongor,[b] Bálint Sztáray,[bd] Leo Meerts,[g] Dana Nachtigallová,*[e]
Pavel Hobza,[e] Mario Barbatti,[f] Hans Lischka*[ef] and Mattanjah S. de Vries*[c]

Received 1st September 2009, Accepted 9th February 2010
First published as an Advance Article on the web 8th April 2010
DOI: 10.1039/b917852j

To explore the excited state dynamics of pyrimidine derivatives, we performed a combined experimental and theoretical study. We present resonant two-photon ionization (R2PI) and IR-UV double resonance spectra of 2,4-diaminopyrimidine and 2,6-diaminopurine seeded in a supersonic jet by laser desorption. For 2,4-diaminopyrimidine ($S_0 \rightarrow S_1$ 34 459 cm^{-1}), we observed only the diamino tautomer with an excited state lifetime bracketed between experimental limits of 10 ps and 1 ns. For 2,6-diaminopurine, we observed two tautomers, the 9H- ($S_0 \rightarrow S_1$ 34 881 cm^{-1}) and 7H- ($S_0 \rightarrow S_1$ 32 215 cm^{-1}) diamino forms, with excited state lifetimes of 6.3 ± 0.4 ns and 8.7 ± 0.8 ns, respectively. We investigated the nature of the excited state of 2,4-diaminopyrimidine by means of multi-reference *ab initio* methods. The calculations of stationary points in the ground and excited states, minima on the S_0/S_1 crossing seam and connecting reaction paths show that several paths with negligible barriers exist, allowing ultrafast radiationless deactivation if excited at energies slightly higher than the band origin. The sub-nanosecond lifetime found experimentally is in good agreement with this finding.

Introduction

Gas phase laser spectroscopy provides the means to study the intrinsic properties of biologically relevant molecules in isolation. Such studies on RNA and DNA bases have revealed unique photophysical properties that are sensitive to subtle structural differences. In many cases, the biologically most relevant tautomeric form has a sub picosecond excited state lifetime, while other *tautomeric forms of the same compound* are much longer lived.[1,2] We have even found that the Watson–Crick structure, adopted by the guanine-cytosine (GC) base pair in DNA, appears to have a much shorter excited state lifetime than other *structures of the same base pair*.[3] Theoretical models explain these short lifetimes by a rapid internal conversion in which the excited state (S_1) is coupled to the ground state (S_0) *via* pathways with no or a very small barrier leading to conical intersections.[4] For the longer lived structures, small differences in relative energies cause the existence of barriers that lead to discrete spectra and lifetimes that can be two orders of magnitude longer. This rapid internal conversion pathway provides selected isomers with significantly enhanced photochemical stability, absent in the other longer lived structures. It is conceivable that these differences between excited state lifetimes of different bases and base-pair structures could have played a significant role in prebiotic chemistry.[3]

The five naturally occurring nucleic acid bases[5–9] exhibit an ultrafast excited state relaxation in the gas phase. For DNA bases it has been shown[1,10–24] that the energetically lowest conical intersections responsible for fast deactivation to the ground state are characterized by ring puckering modes. The most favorable ring puckering conical intersections result from the change of the HC6C5R (R = H, CH_3) dihedral angle in uracil and thymine and the HN1C2H dihedral angle in adenine. This model also explains why by contrast 2-aminopurine, in which the C2 position is substituted by the amino group, has a long excited state lifetime and strong fluorescence.[25–27] Alternatively, the puckering at the C6 atom was also suggested to be responsible for adenine relaxation.[28]

Recently, surface-hopping dynamics studies of 4-aminopyrimidine (4-APy)[29–31] and 9H-adenine[24] showed that while the former relaxes into the ground state *via* different conical

---

[a] *Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA. E-mail: dana.nachtigallova@uochb.cas.cz, hans.lischka@univie.ac.at, devries@chem.ucsb.edu; Fax: (+1) 805-893-4120; Tel: (+1) 805-893-5921*
[b] *Institute of Chemistry, Eötvös Loránd University Budapest, 1/A Pázmány P. stny., Hungary 1117*
[c] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA-93106-9510, USA*
[d] *Department of Chemistry, University of the Pacific, Stockton, CA-95211, USA*
[e] *The Institute of Organic Chemistry and Biochemistry, Flemingovo nám., 2, 166 10 Praha 6, Czech Republic*
[f] *Institute for Theoretical Chemistry, University of Vienna, Waehringerstrasse 17, A1090 Vienna, Austria*
[g] *Molecular and Biophysics Group, Institute for Molecules and Materials, Radboud University, 6500 GL Nijmegen, The Netherlands*

† Electronic supplementary information (ESI) available: The calculated vertical ionization potentials for all the 2,4-diaminopyrimidine tautomers (Fig. S1 and Table S1). The vertical excitation energies calculated at the RICC2 method with various basis sets (Table S2). The interpolation curves between the S1min_C2 and S1min_C6 minima towards various MXS structures calculated at the CASSCF and MR-CISD(17)+Q methods (Fig. S2). This material is available free of charge on the Internet. See DOI: 10.1039/b917852j

14

Electronic splitting in the excited states of DNA base homodimers and -trimers: an evaluation of short-range and Coulombic interactions†

Dana Nachtigallová,[a] Pavel Hobza[a] and Hans-Hermann Ritze*[b]

Received 14th April 2008, Accepted 13th June 2008
First published as an Advance Article on the web 30th July 2008
DOI: 10.1039/b806323k

The nature of the electronic interactions of the stacked nucleic-acid bases (adenine, thymine, cytosine, and uracil) in homodimer and -trimer complexes in their electronically excited states was investigated and analysed in terms of orbital-overlap and Coulombic interactions. The mutual orientations of the adjacent bases were selected so as to correspond to the A- and B-DNA conformations. The extent of the electronic interaction is larger for the former conformation. It is shown that the orbital-overlap interactions at the distance of two bases relevant to the DNA structure do not contribute significantly to the overall electronic coupling. Only the states which are caused by the ($\pi \rightarrow \pi^*$) transitions manifest an electronic coupling.

1. Introduction

The phenomenon of the delocalisation of excited states, the electronic coupling and the transfer of excitation energy between the adjacent nucleic-acid bases in the stacked conformation has recently become the subject of many discussions. These processes are closely related to energy migration along the nucleic-acid strands, which may be a possible mechanism through which nucleic acids protect themselves against UV damage. The behaviour of nucleic acids in the excited states is very complex. The dynamics of nucleic acids in the excited states are affected by numerous factors, including *e.g.* the plasticity of the sugar–phosphate backbone, which influences the mutual orientation of bases, the lifetime of the excited states and the presence of water molecules, which are bonded directly to the nucleic-acid bases. It is thus difficult to identify the extent of the electronic coupling between the stacked nucleic-acid bases, which is responsible for both the formation of excimers and the energy migration.

The development of time-resolved fluorescence spectroscopy with femtosecond resolution makes it possible to investigate the excited states of nucleic-acid bases and the nature of their interactions. The features observed in the spectra can be explained by the presence of excited states localised on monomers, excimer formation and the existence of excitons. The effects of base sequence, the size of the DNA duplex and the conformation on the spectra were examined.[1–8] Spectral manifestation of the exciton formation was observed for adenine and cytosine dimers but not for thymine and guanine dimers.[8] Similar differences with respect to excimer formation were observed also for adenine and cytosine, as well as thymine and guanine oligonucleotides.[9]

Experiments performed with the alternating (dA·dT), (dG·dC), and non-alternating dA and dT polymers or oligomers have shown that the efficiency of excimer formation depends on the base sequence.[3,10–12] In particular, the transient absorption signals associated with the excimer formation decay faster in the case of oligomers with (dA·dT) alternating sequences. The slow component of the transient signals of non-alternating sequences in $(dA)_{18}\cdot(dT)_{18}$ was very similar to that observed for $(dA)_{18}$. It was suggested that the excited states are initially localised, with the subsequent ultrafast formation of excimers.[3]

Based on the steady-state absorption and fluorescence spectra of poly(dA)·poly(dT), it was suggested that the excited states are delocalised over several bases.[4,13] Onidas *et al.* have studied the fluorescence spectra of alternating A–T polymers and oligomers and compared them to those for the homopolymeric sequences $(dA)_n\cdot(dT)_n$.[14] The steady-state fluorescence spectra for these two types of oligomers and polymers were different. The differences in the spectra were explained by a population of exciton states after the absorption, followed by an ultrafast intra-band scattering and emission of monomers and excitons. In the case of the alternating $(dAdT)_n\cdot(dAdT)_n$, these emitting states were quenched by excimers characterised by long-lived excited states. The nature of the energy transfer was investigated theoretically for the model B-DNA poly(dA)·poly(dT) duplex.[15] In accord with experimental findings, it was suggested that for exciton dynamics the intra-strand stacking interactions are much more important than those between two chains. The calculations also predict that, unlike the exciton located on adenosine, the thymidine exciton decomposes into electron–hole pairs.

Miannay *et al.* have recently reported the results of a femtosecond study of guanine–cytosine DNA double helices.[5] In poly(dGdC)·poly(dGdC), excited states relax faster than the respective monomers, unlike A–T duplexes, characterised by a lengthening of the excited-state lifetime. Nevertheless, signs of the electron transfer along the helix have been detected also for this system.

---

[a] *Center for Biomolecules and Complex Molecular Systems, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i. Flemingovo nám. 2, 166 10 Praha 6, Czech Republic*
[b] *Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born-Strasse 2A, D-12489 Berlin, Germany. E-mail: ritze@mbi-berlin.de*

† Electronic supplementary information (ESI) available: Vertical excitation energies and details of various approximations for the transition Coulomb interaction. See DOI: 10.1039/b806323k

Electronic coupling in the excited electronic state of stacked DNA base homodimers†

Hans-Hermann Ritze,[b] Pavel Hobza[a] and Dana Nachtigallová*[a]

Received 15th December 2006, Accepted 12th February 2007
First published as an Advance Article on the web 26th February 2007
DOI: 10.1039/b618382d

The nature of the electronic coupling of stacked nucleic acid bases adenine (A), thymine (T), and cytosine (C), in A–A, T–T, and C–C complexes in their excited states was investigated; a different character of the electronic coupling for the T–T complex was shown.

The nature of the excited states of DNA bases, in particular, the extent of excited state delocalization along the double helix has been the subject of much discussion. The lack of any significant spectral shift in UV spectra[1] led to the opinion that the excited states are localized on a single base contrary to theoretically suggested delocalization of the excited states.[2] Only recently has the use of time-resolved fluorescence spectroscopy with femtosecond resolutions of DNA oligomers[3–11] allowed the reinvestigation of the problem of excited states delocalization. Based on the results of these studies, in particular, on single and double helices of A and T, it is now assumed that the excited states are delocalized over several bases. Slow components which appear in time-resolved transient absorption spectra of $(dA)_{18}$, $(dA)_{18} \cdot (dT)_{18}$, and $(dAdT)_9 \cdot (dAdT)_9$ were associated with the adenine excimers.[3]

The question of excited states delocalization becomes important when discussing the photostability of DNA with respect to UV damage. One of the suggested operative mechanisms is linked to the very short lifetime of excited states of isolated nucleic acid bases[12] which is attributed to non-radiative relaxation to the ground state. Several mechanisms were suggested for this non-radiative decay.[13–17]

An alternative explanation of how DNA protects itself from UV damage is the fast transfer of excitation energy which prevents the localization of electronic energy and subsequent photochemical reaction. It has already been suggested that the differences in the photochemistry of poly(A) and poly(dA) homopolymers are the result of different stacking of the two adjacent bases.[18] While poly(A) which possesses A-type DNA conformation shows almost no reactivity in the excited state, poly(dA) with B-type DNA conformation is able to form dimeric photoproducts. The photodimerization process of two adjacent pyrimidine bases is a problem which attracts even more attention. There are two experimental observations which are subject to theoretical investigation: (i) upon UVC irradiation *cis,syn*-cyclobutane dimer is most frequently formed between two adjacent T bases,[19] (ii) oligonucleotides in an A-type conformation are more UV resistant than in B-type conformation. Also in this case the question of the role of delocalization was raised.[5] The mechanism of the photodimerization process of adjacent thymines was investigated theoretically using a time-dependent DFT method.[20–23]

Due to its structure, the electronic coupling and hence the nature of excited state delocalization results from both the orbital overlap in the short-range limit and interaction of transition dipole moments (dipole–dipole interaction) in the intermediate-range limit.[24] It is a generally accepted view that the extent of the delocalization depends on the base sequence as well as on the structure of the DNA helix which effects their mutual orientation.

Clearly, electron delocalization is a very complex problem in which several aspects, including the base sequence and respective orientation of the bases controlled by the sugar–phosphate structure play an important role in both the short-range and intermediate-range limits. The nature of excited states within the DNA helix has been studied theoretically within the framework of the exciton theory.[8–10] In these studies, the electronic coupling due to the dipole–dipole interaction only was investigated. In agreement with experiment, it was suggested that the excited states are delocalized over at least two bases. Very recently, Olaso-Gonzáles *et al.* using *ab initio* complete active space second order perturbation theory (CASPT2) studied the lowest excited state of two cytosine bases in the stacked conformation.[25] The excimer formation was predicted which is suggested to be responsible for redshifted fluorescence observed in cytosine oligonucleotides.[26]

When two chromophores interact in the excited state, the resulting transition energies are shifted with respect to the energy of the monomer and the transition energies split. For symmetrical arrangements this splitting is a measure of the electronic coupling between the two chromophores (bases) in the excited state.[24]

For non-symmetric arrangements of the monomers, the resulting energy splitting is due to both, a net electronic

---

[a] *Center for Biomolecules and Complex Molecular Systems, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo na'm. 2, 166 10 Praha 6, Czech Republic. E-mail: dana.nachtigallova@uochb.cas.cz*
[b] *Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born-Strasse 2A, D-12489 Berlin, Germany. E-mail: ritze@mbi-berlin.de*

† Electronic supplementary information (ESI) available: Geometries of stacked DNA bases (Fig. S1–S3); excitation energies (in eV) and their splitting (ΔE) of model ethylene–dimer and ethylene–acetylene systems in stacked conformation (Tables S1 and S2). See DOI: 10.1039/b618382d

16

Photochemical &
Photobiological Sciences

RSCPublishing

PAPER

Cite this: *Photochem. Photobiol. Sci.*, 2013, **12**, 1496

The effect of dimerization on the excited state behavior of methylated xanthine derivatives: a computational study†

Dana Nachtigallová,*[a] Adelia J. A. Aquino,[b,c] Shawn Horn[b] and Hans Lischka*[b,d]

Received 4th March 2013,
Accepted 20th June 2013

DOI: 10.1039/c3pp50077b

www.rsc.org/pps

The behavior of monomers and dimers of methylated xanthine derivatives in their excited states is investigated by means of the ADC(2), CASSCF, and CASPT2 methods. The results of the calculations of stationary points in the ground and excited states, minima on the S_0/S_1 crossing seams and the relaxation pathways are used to provide the interpretation of experimental observations of the monomer xanthine derivatives. The effect of dimerization on the excited state properties is studied for various relative orientations of the monomers in the dimer complexes in comparison with the relevant monomer species. A significant stabilization in the excited state minima of dimers is observed. These can act as trapping sites. Various types of conical intersections, with both localized and delocalized characters of wavefunctions, have been found, mainly energetically above the lowest bright excited state in the FC region. In addition, structures with the bonds formed between the two monomers were also found on the crossing seams. The possibility of ultrafast relaxation *via* these conical intersections is discussed.

Introduction

In the last decade, impressive progress in the field of photochemistry of nucleic acids and related molecular systems could be observed. As UV irradiation can cause serious damage to DNA, leading to modifications in the genetic code, this topic is highly important. The picosecond and subpicosecond excited state photodynamics of isolated naturally occurring nucleobases was investigated experimentally[1–6] and their relaxation mechanisms were explained by a nonadiabatic internal conversion *via* conical intersections.[7–19] These processes are fairly well understood now, even though many interesting detailed questions still await their solution. The excited state behavior of nucleobases becomes much more complex when embedded in the structure of nucleic acids. The relaxation occurs on a time scale of picoseconds up to hundreds of picoseconds. Relaxation mechanisms mediated by both, the formation of intra-strand delocalized excitons and excimer/exciplex complexes, including charge transfer excited states,[20–28] and interstrand proton transfer, were discussed.[29–32]

To reduce this complexity, the photodynamics of dinucleotide analogues has been investigated (*e.g.* ref. 33) with the goal of transferring the experience obtained with such simpler problems to the more complex situation found in DNA. In this regard, nucleic acid analogues play an important role because of the larger choice of compounds available and the interest in replacing natural counterparts in DNA by these candidates. Xanthine (3,7-dihydro-purine-2,6-dione) is one important representative of such nucleic acid analogues.

Recently, excited state lifetimes of xanthine (*X*) and methylated derivatives (*theophylline (1,3-diMet-X), theobromine (3,7-diMet-X) and caffeine (1,3,7-triMet-X)*) were determined using femtosecond transient absorption spectroscopy in aqueous and acetonitrile solutions.[34] The observed spectra revealed that in water all of these species relax to the electronic ground state on a subpicosecond time scale. Resonant two-photon ionization (R2PI) and IR-UV double resonance spectroscopy performed for the same methylated species in the gas phase[33] and xanthine itself[35] were all sharp and vibrationally resolved, suggesting a long excited state lifetime. Computational studies based on the complete active space with perturbation theory to the second order (CASPT2) and approximate coupled cluster singles-and-doubles method (CC2) calculations assigned the gas phase monomer spectra to the *7H-diketo* tautomer of

---

[a] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 166 10 Prague 6, Czech Republic.*
E-mail: dana.nachtigallova@uochb.cas.cz

[b] *Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, USA*

[c] *Institute for Soil Research, University of Natural Resources and Life Sciences Vienna, Peter-Jordan-Strasse 82, A 1190 Vienna, Austria*

[d] *Institute for Theoretical Chemistry, University of Vienna, Währingerstr. 17, 1090 Vienna, Austria*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3pp50077b

The Charge-Transfer States in a Stacked Nucleobase Dimer Complex: A Benchmark Study

ADÉLIA J. A. AQUINO,[1,2] DANA NACHTIGALLOVA,[3] PAVEL HOBZA,[3] DONALD G. TRUHLAR,[4]
CHRISTOF HÄTTIG,[5] HANS LISCHKA[1,3]

[1]*Institute for Theoretical Chemistry, University of Vienna, Währinger Straße 17, A-1090 Vienna, Austria*

[2]*Institute of Soil Research, University of Natural Resources and Life Sciences Vienna, Peter-Jordan-Straße 82, A-1190 Vienna, Austria*

[3]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems, Flemingovo nam. 2, 166 10 Prague 6, Czech Republic*

[4]*Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431*

[5]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44801 Bochum, Germany*

Received 9 August 2010; Revised 27 September 2010; Accepted 1 October 2010
DOI 10.1002/jcc.21702

Abstract: Electronic singlet excitations of stacked adenine–thymine (AT) and guanine–cytosine (GC) complexes have been investigated with respect to local excitation and charge-transfer (CT) characters. Potential energy curves for rigid displacement of the nucleobases have been computed to establish the distance dependence of the CT states. The second-order algebraic diagrammatic construction [ADC(2)] method served as reference approach for comparison to a selected set of density functionals used within the time-dependent density functional theory (TD-DFT). Particular attention was dedicated to the performance of the recently developed family of M06 functionals. The calculations for the stacked complexes show that at the ADC(2) level, the lowest CT state is S_6 for the AT and as S_4 for the GC pair. At the reference geometry, the actual charge transferred is found to be 0.73 *e* for AT. In case of GC, this amount is much smaller (0.17 *e*). With increasing separation of the two nucleobases, the CT state is strongly destabilized. The M06-2X version provides a relatively good reproduction of the ADC(2) results. It avoids the serious overstabilization and overcrowding of the spectrum found with the B3LYP functional. On the other hand, M06-HF destabilizes the CT state too strongly. TD-DFT/M06-2X calculations in solution (heptane, isoquinoline, and water) using the polarizable continuum model show a stabilization of the CT state and an increase in CT character with increasing polarity of the solvent.

J Comput Chem 32: 1217–1227, 2011

Key words: charge transfer; excited states; coupled cluster; DFT; stacked nucleobases

---

Additional Supporting Information may be found in the online version of this article.

Correspondence to: A. J. A. Aquino; e-mail: adelia.aquino@univie.ac.at or H. Lischka; e-mail: hans.lischka@univie.ac.at

Contract/grant sponsor: Austrian Science Fund [Special Research Programs F16 (Advanced Light Sources) and F41 (ViCoM)] and contract/grant number: P18411-N19

Contract/grant sponsor: German Research Foundation (priority program SPP 1315); contract/grant number: GE 1676/1-1

Contract/grant sponsors: Ministry of Education of the Czech Republic (Center for Biomolecules and Complex Molecular Systems, LC512) and Praemium Academiae of the Academy of Sciences of the Czech Republic awarded to PH in 2007

Contract/grant sponsor: Institute of Organic Chemistry and Biochemistry of the Academy of Sciences of the Czech Republic; contract/grant number: research project Z40550506

Contract/grant sponsor: U. S. National Science Foundation; contract/grant number: CHE09-56776

Contract/grant sponsor: Vienna Scientific Cluster; contract/grant numbers: 70019 and 70151

JCTC Journal of Chemical Theory and Computation
Article
pubs.acs.org/JCTC

Singlet L_a and L_b Bands for N-Acenes (N = 2−7): A CASSCF/CASPT2 Study

Fernanda Bettanin,[†] Luiz F. A. Ferrão,[*,†] Max Pinheiro, Jr.,[†] Adélia J. A. Aquino,[‡,§] Hans Lischka,[‡,§] Francisco B. C. Machado,[*,†] and Dana Nachtigallova[*,∥,⊥]

[†]Departamento de Química, Instituto Tecnológico da Aeronáutica, São José dos Campos, 122228-900 São Paulo, Brazil

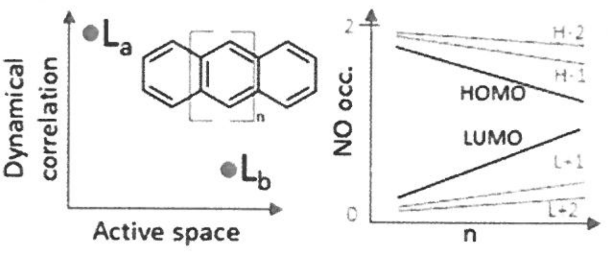
[‡]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States

[§]School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin 300072, P.R. China

[∥]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic

[⊥]Regional Center of Advanced Technologies and Materials, Department of Physical Chemistry, Palacky University, Olomouc 77146, Czech Republic

Supporting Information

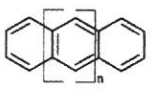


ABSTRACT: In this work CASPT2 calculations of polyacenes (from naphthalene to heptacene) were performed to find a methodology suitable for calculations of the absorption spectra, in particular of the L_a (B_{2u} state) and L_b (B_{3u} state) bands, of more extended systems. The effect of the extension of the active space and of freezing σ orbitals was investigated. The MCSCF excitation energy of the B_{2u} state is not sensitive to the size of the active space used. However, the CASPT2 results depend strongly on the amount of σ orbitals frozen reflecting the ionic character of the B_{2u} state. On the other hand, the excitation energies of the B_{3u} state are much more sensitive to the size of the active space used in the calculations reflecting its multiconfigurational character. We found a good agreement with experimental data for both bands by including 14 electrons in 14 π orbitals in the active space followed by the CASPT2(14,14) perturbation scheme in which both σ and π orbitals are included.

1. INTRODUCTION

Due to the promising potential applications of materials which contain π-conjugated systems[1−8] to be used as chemical sensors, organic semiconductors, in spintronics and nonlinear optics, a large number of studies on graphene and its model systems appeared recently in the literature.[9−15] The electronic properties of polyacenes (PACs, Scheme 1) not only are very attractive for material science,[16−24] but also they can serve as a model system for studying the properties of ground and excited states of extended π systems[23,25−42] by means of theoretical methods.

Scheme 1. Structure of Studied Polyacenes (n = 0−5)



PACs possess D_{2h} symmetry with a totally symmetric (A_{1g}) electronic ground state. The two low-lying excited states in the absorption spectra are short-axis polarized (L_a) and long-axis polarized (L_b) states of B_{2u} and B_{3u} symmetries, respectively.[33] The two lowest excited states of gerade symmetry, not seen in the absorption spectra, are of A_{1g} and B_{1g} symmetries. According to previous theoretical results,[18,29,31−33,37−39,43−46] two main conclusions can be drawn from these calculations: (1) the multireference character of the ground state electronic configuration increases with increasing number of fused benzene rings and (2) doubly excited configurations contribute to the wave functions of the low-lying excited states. For polyacenes larger than tetracene these configurations need to be included to correctly describe the ordering of the excited state of A_g and B_{3u} symmetries observed experimentally.[44]

A multiconfigurational character of the wave function was found[37,43] for the first excited state (B_{3u}) of naphthalene, resulting from a linear combination of HOMO−1 → LUMO and HOMO → LUMO+1 configurations, while the wave function of the second excited state (B_{2u}) corresponds almost exclusively to a HOMO → LUMO excitation. For acenes larger than naphthalene, the B_{2u} and B_{3u} states change their energy ordering. The A_{1g} state is best described by the double excitation HOMO^2 → LUMO^2. The B_{1g} state wave function has large contributions from the singly excited configurations

Received: March 21, 2017
Published: July 18, 2017

DOI: 10.1021/acs.jctc.7b00302
J. Chem. Theory Comput. 2017, 13, 4297−4306

The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

High-level theoretical benchmark investigations of the UV-vis absorption spectra of paradigmatic polycyclic aromatic hydrocarbons as models for graphene quantum dots

Cite as: J. Chem. Phys. 150, 124302 (2019); doi: 10.1063/1.5086760
Submitted: 22 December 2018 • Accepted: 3 March 2019 •
Published Online: 26 March 2019

Baimei Shi,[1] Dana Nachtigallová,[2,3,a)] Adélia J. A. Aquino,[1] Francisco B. C. Machado,[4] and Hans Lischka[1,a)]

AFFILIATIONS

[1] School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin 300072, People's Republic of China
[2] Institute of Organic Chemistry and Biochemistry v.v.i., The Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic
[3] Regional Centre of Advanced Technologies and Materials, Palacký University, 78371 Olomouc, Czech Republic
[4] Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos, São Paulo 12228-900, Brazil

[a)] **Authors to whom correspondence should be addressed:** hans.lischka@univie.ac.at and dana.nachtigallova@uochb.cas.cz

ABSTRACT

Five paradigmatic polycyclic aromatic hydrocarbons (PAHs) (pyrene, circum-1-pyrene, coronene, circum-1-coronene, and circum-2-coronene) are used for studying the performance of three single-reference methods {scaled opposite-spin-algebraic diagrammatic construction to second-order [SOS-ADC(2)], time-dependent (TD)-B3LYP, and TD-Coulomb-attenuating method (CAM)-B3LYP} and three multireference (MR) methods [density functional theory/multireference configuration interaction (DFT/MRCI), strongly contracted-*n*-electron valence state perturbation theory to second order (NEVPT2), and spectroscopy oriented configuration interaction (SORCI)]. The performance of these methods was evaluated by comparison of the calculated vertical excitation energies with experiments, where available. DFT/MRCI performs best and thus was used as a benchmark for other approaches where experimental values were not available. Both TD-B3LYP and NEVPT2 agree well with the benchmark data. SORCI performs better for coronene than for pyrene. SOS-ADC(2) does reasonably well in terms of excitation energies for smaller systems, but the error increases somewhat as the size of the system gets bigger. The natural transition orbital analysis for SOS-ADC(2) results indicated that at least two configurations were essential to characterize most of the lower-case electronic states. TD-CAM-B3LYP gives the largest errors for excitation energies and also gives an incorrect order of the lowest two states in circum-1-pyrene. A strong density increase of dark states was observed in the UV spectra with increasing size except for the lowest few states which remained well separated. An extrapolation of the UV spectra to infinite PAH size for S_1, S_2, and the first bright state based on the coronene series was made. The extrapolated excitation energies closest to experimental measurements on graphene quantum dots were obtained by TD-CAM-B3LYP.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), conjugated aromatic molecules composed of fused benzenoid rings, have aroused widespread interest among scientists due to their important role in many fields ranging from chemistry[1] and materials science[2] to astrochemistry.[3] In particular, PAHs are also regarded as a cut out and model of graphene, especially in the case of the larger PAHs denoted as nanographenes or graphene quantum dots (GQDs),[4–6] which are promising materials being used in

ACSNANO
www.acsnano.org

Graphitic Nitrogen Triggers Red Fluorescence in Carbon Dots

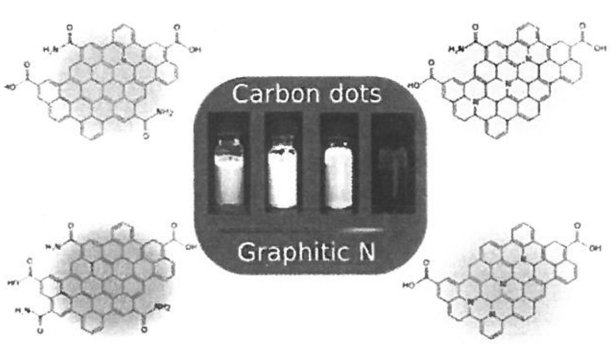
Kateřina Holá,[†] Mária Sudolská,[†] Sergii Kalytchuk,[†] Dana Nachtigallová,[†,‡] Andrey L. Rogach,[§] Michal Otyepka,[†] and Radek Zbořil*[,†]

[†]Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacký University Olomouc, Šlechtitelů 27, 78371 Olomouc, Czech Republic

[‡]Intitute of Organic Chemistry and Biochemistry, The Czech Academy of Sciences, Flemingovo nám. 2, 16000 Prague 6, Czech Republic

[§]Department of Materials Science and Engineering and Center for Functional Photonics (CFP), City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong S.A.R.

Ⓢ *Supporting Information*



ABSTRACT: **Carbon dots (CDs) are a stable and highly biocompatible fluorescent material offering great application potential in cell labeling, optical imaging, LED diodes, and optoelectronic technologies. Because their emission wavelengths provide the best tissue penetration, red-emitting CDs are of particular interest for applications in biomedical technologies. Current synthetic strategies enabling red-shifted emission include increasing the CD particle size (sp^2 domain) by a proper synthetic strategy and tuning the surface chemistry of CDs with suitable functional groups (*e.g.*, carboxyl). Here we present an elegant route for preparing full-color CDs with well-controllable fluorescence at blue, green, yellow, or red wavelengths. The two-step procedure involves the synthesis of a full-color-emitting mixture of CDs from citric acid and urea in formamide followed by separation of the individual fluorescent fractions by column chromatography based on differences in CD charge. Red-emitting CDs, which had the most negative charge, were separated as the last fraction. The trend in the separation, surface charge, and red-shift of photoluminescence was caused by increasing amount of graphitic nitrogen in the CD structure, as was clearly proved by XPS, FT-IR, Raman spectroscopy, and DFT calculations. Importantly, graphitic nitrogen generates midgap states within the HOMO−LUMO gap of the undoped systems, resulting in significantly red-shifted light absorption that in turn gives rise to fluorescence at the low-energy end of the visible spectrum. The presented findings identify graphitic nitrogen as another crucial factor that can red-shift the CD photoluminescence.**

KEYWORDS: *nitrogen-doped, graphene dots, red fluorescence, fluorescence mechanism, band-gap tuning*

Carbon dots (CDs) attract broad scientific interest owing to their attractive fluorescence properties. They are resistant to photobleaching akin to traditional semiconductor quantum dots[1,2] but still possess a great safety profile.[3] Therefore, they have found wide utilization in biomedical fields, *e.g.*, cell labeling, optical imaging, drug delivery, and biosensing.[4−9] They have also been applied in various technologies, *e.g.*, light-emitting diodes,[10] water splitting,[11] and photocatalysis.[12] In recent years, many synthetic procedures have been developed to prepare and tune the optical properties of CDs. Since the discovery of this material in 2004, mainly blue, green, and yellow fluorescent CDs have been reported.[1,2] However, very few reproducible synthetic strategies for red fluorescent CDs have been published.[13,14] Red-emitting CDs are particularly suitable for biomedical applications because red light shows the best tissue penetration. In addition, red CDs can provide the missing building block for a full-color-emitting spectrum, *e.g.*, for white-light-emitting diodes. Therefore, efficient and reproducible synthetic pathways for the production of red fluorescent CDs can advance applications of CDs in many scientific and industrial areas.

Recently, attention has been given to understanding the origin of CD photoluminescence because knowledge in this field may support the rational design of CD optical properties.

Received: September 8, 2017
Accepted: November 14, 2017
Published: November 14, 2017

DOI: 10.1021/acsnano.7b06399
ACS Nano 2017, 11, 12402−12410

Applied Materials Today 22 (2021) 100924

Contents lists available at ScienceDirect

Applied Materials Today

journal homepage: www.elsevier.com/locate/apmt

Progress and challenges in understanding of photoluminescence properties of carbon dots based on theoretical computations

Michal Langer[a,b], Markéta Paloncýová[a], Miroslav Medveďa[a], Martin Pykal[a], Dana Nachtigallová[a,c], Baimei Shi[d], Adélia J.A. Aquino[d,e], Hans Lischka[d,f], Michal Otyepka[a,*]

[a] Regional Centre of Advanced Technologies and Materials, Faculty of Science, Palacký University Olomouc, Šlechtitelů 27, Olomouc 783 71, Czech Republic
[b] Department of Physical Chemistry, Faculty of Science, Palacký University Olomouc, 17. listopadu 12, Olomouc 711 46, Czech Republic
[c] The Czech Academy of Sciences, Institute of Organic Chemistry and Biochemistry v.v.i., Prague 6 166 10, Czech Republic
[d] School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China
[e] Department of Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, USA
[f] Department of Chemistry and Biochemistry, Texas Tech University Lubbock, TX 79409-1061, USA

ARTICLE INFO

Article history:
Received 27 October 2020
Revised 1 December 2020
Accepted 21 December 2020

Keywords:
Carbon dots
Structure
Absorption
Photoluminescence
Theoretical calculations

ABSTRACT

Carbon dots (CDs), including graphene quantum dots, carbon nanodots, carbon quantum dots, and carbonized polymer dots, belong to extensively studied nanomaterials with a very broad application potential resulting from their bright photoluminescence (PL), high (photo)stability, low toxicity and great biocompatibility. However, the design of CDs with tailored properties is still hampered by a fairly limited understanding of the CD PL, which stems from their rather complex structure and variability of the PL centers. Theoretical calculations provide valuable insights into the nature of the excited states and the source of PL. In this review, we focus on state-of-the-art theoretical methods for the description of absorption and PL of CDs and their limitations, along with providing an overview of theoretical studies addressing structural models and the electronic structure of various types of CDs in the context of their overall optical properties. Besides the assessment of the current state of knowledge, we also highlight the opportunity for further advancements in the field.

1. Introduction

1.1. Discovery and definition of carbon dots

Nanosized carbon-based materials, such as fullerenes, nanotubes, and graphene, have attracted attention of scientists owing to their unique physicochemical properties often very different from those of the original bulk material. In 2004, Xu *et al.* [1] started to write a new exciting chapter on carbon nanostructures by separating a mixture of weakly fluorescent carbon nanoparticles from single-walled carbon nanotubes obtained from arc-discharge soot. Since then, carbon dots (CDs), as these carbon-based fluorescent nanoparticles (with at least one dimension smaller than 10 nm) are nowadays referred to, have expanded into a large class of metal-free nanomaterials with significant and tuneable photoluminescence (PL). Other unique properties, in particular, non/low-toxicity, biocompatibility, dispersibility in a wide range of solvents, biodegradability, low-cost, facile and scalable synthesis, predispose CDs for plethora of environment-friendly applications in biomedical imaging and sensing [2–4], cancer therapy [5], or theranostics [6], anti-counterfeiting [7], light-emitting devices [8–11], optoelectronic devices [12–15], photocatalysis [16] and functional materials [17,18].

1.2. Synthesis of CDs

In general, the CDs can be prepared by employing either top-down or bottom-up approaches [12]. The top-down methods usually require harsh conditions (strong oxidants, concentrated acids, and high temperatures) or severe physical techniques (laser ablation, arc discharge and nanolithography) to cut, decompose and/or exfoliate bulk carbonaceous materials (e.g., graphite, graphene oxide, activated carbon, soot, carbon nanotubes) into carbon nanoparticles [19–27]. On the other hand, the bottom-up strategies such as stepwise organic synthesis, hydrothermal/solvothermal synthesis, and chemical vapor deposition and microwave-assisted treatments can utilize a large variety of simple organic precursors [28,29]. The optimization of reagents and reaction conditions yielded CDs with significantly enhanced PL quantum yields (QYs) which were mainly attributed to heteroatom doping effects, surface functionalities, and, last but not least, the presence of molecular fluorophores

---

* Corresponding author.

https://doi.org/10.1016/j.apmt.2020.100924

PCCP

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2020, 22, 22003

Tuning the UV spectrum of PAHs by means of different N-doping types taking pyrene as paradigmatic example: categorization *via* valence bond theory and high-level computational approaches†

Xin Shao,[a] Adelia J. A. Aquino,[ab] Michal Otyepka,[c] Dana Nachtigallová*[cd] and Hans Lischka*[ae]

Tuning of the electronic spectra of carbon dots by means of inserting heteroatoms into the π-conjugated polycyclic aromatic hydrocarbon (PAH) system is a popular tool to achieve a broad range of absorption and emission frequencies. Especially nitrogen atoms have been used successfully for that purpose. Despite the significant progress achieved with these procedures, the prediction of specific shifts in the UV-vis spectra and the understanding of the electronic transitions is still a challenging task. In this work, high-level quantum chemical methods based on multireference (MR) and single-reference (SR) methods have been used to predict the effect of different nitrogen doping patterns inserted into the prototypical PAH pyrene on its absorption spectrum. Furthermore, a simple classification scheme based on valence bond (VB) theory and the Clar sextet rule in combination with the harmonic oscillator measure of aromaticity (HOMA) index was applied to arrange the different doping structures into groups and rationalize their electronic properties. The results show a wide variety of mostly redshifts in the spectra as compared to the pristine pyrene case. The most interesting doping structures with the largest red shifts leading to absorption energies below one eV could be readily explained by the occurrence of diradical VB structures in combination with Clar sextets. Moreover, analysis of the electronic transitions computed with MR methods showed that several of the low-lying excited states possess double-excitation character, which cannot be realized by the popular SR methods and, thus, are simply absent in the calculated spectra.

Received 18th May 2020,
Accepted 17th September 2020

DOI: 10.1039/d0cp02688c

rsc.li/pccp

1. Introduction

Due to their outstanding optical properties, carbon dots (CD) constitute a fascinating new carbon-based material with interesting applications in materials science, chemistry, biosensing and several other fields.[1–5] Their chemical modification, which includes also chemical doping, provides a promising strategy to modulate their electronic properties which should convert them to materials with even better performance than their pristine counter-partners.[6] In particular, nitrogen doping changes the electronic properties of CDs, which can be efficiently used to design systems such as sensors,[7] electrocatalysts in redox reactions,[8–12] systems with capabilities of electrochemical energy storage,[13] photocatalysts,[14–17] and battery constructions.[18] Their optical properties with the photoluminescence quantum yield up to 75% make them efficient fluorescence probes[19–23] and light-emitting diodes.[24] In this context, the red-shift of the fluorescence is of great relevance *e.g.* for bioimaging applications because near infra-red light exhibits deeper tissue penetration.[25]

Despite the large potential of just-mentioned N-doped CDs, understanding of the optical spectra and finding materials which possess appropriately red-shifted UV and fluorescence properties represent still a challenging task for experimental as

---

[a] *School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, P. R. China. E-mail: hans.lischka@univie.ac.at*

[b] *Department of Mechanical Engineering, Texas Tech University, Lubbock, TX, 79409, USA*

[c] *Regional Centre of Advanced Technologies and Materials, Palacký University, 78371 Olomouc, Czech Republic*

[d] *Institute of Organic Chemistry and Biochemistry v.v.i., The Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic. E-mail: dana.nachtigallova@marge.uochb.cas.cz*

[e] *Department of Chemistry and Biochemistry, Texas Tech University Lubbock, TX 79409-1061, USA*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cp02688c

THE JOURNAL OF
PHYSICAL CHEMISTRY

pubs.acs.org/JPCA

Article

Doping Capabilities of Fluorine on the UV Absorption and Emission Spectra of Pyrene-Based Graphene Quantum Dots

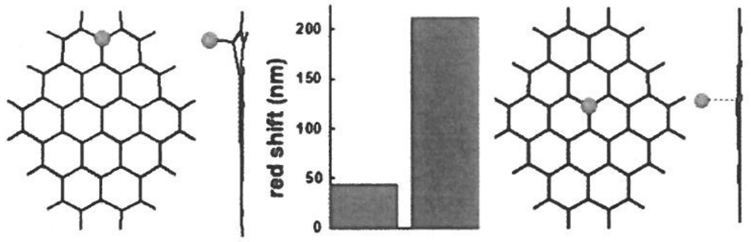
Published as part of The Journal of Physical Chemistry virtual special issue "Josef Michl Festschrift".

Bo Liu, Adelia J. A. Aquino, Dana Nachtigallová,* and Hans Lischka*

Cite This: *J. Phys. Chem. A* 2020, 124, 10954−10966

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



Fluorescence red-shift depends strongly on the F⁻ position

ABSTRACT: Functionalization of quantum carbon dots (QCDs) and graphene quantum dots (GQDs) is a popular way to tune their optical spectra increasing their potential applicability in material science and biorelated disciplines. Based on the experimental observation, functionalization by fluorine atoms induces substantial shifts in absorption and emission spectra and an intensity increase. Understanding of the effects due to fluorine functionalization at the atomic scale level is still challenging due to the complex structure of fluorinated QCDs. In this work, the effect of covalent edge-fluorination and fluorine anion doping on absorption and emission spectra of prototypical polycyclic aromatic hydrocarbons pyrene and circum-pyrene has been investigated. The ways to achieve efficient red-shifts in the UV spectra and obtaining reasonable intensities stood in the focus of the work. High-level quantum chemical methods based on density functional theory/multireference configuration interaction (DFT/MRCI) and single-reference second-order algebraic diagrammatic construction (ADC(2)) and density functional theory (DFT) using the CAM-B3LYP functional have been used for this purpose. The calculations show that doping with the fluoride anion can have significant effects on the electronic spectrum. However, the effect of the fluoride ion is strongly dependent on its position with respect to the QCD. The localization above the GQDs causes large red-shifts to both the absorption and emission of spectra of GQDs, while in-plane localization leads to only negligible shifts and a tendency to dissociation after electronic excitation. Thus, large red-shifts, observed in complexes with F^-, are obtained due to the introduction of new excited states with large CT character not yet been considered previously in this context, although they have the potential to significantly influence the photophysics of quantum dots. Doping by edge fluorination redshifts the spectra only slightly. This study provides insights on fluorine-doped GQDs, which is conducive to promoting its rational design and controllable synthesis.

1. INTRODUCTION

Fluorination of carbon-based materials[1] is a widely investigated way to modify the properties of carbon materials, including graphite,[2] graphene,[3−8] and carbon nanotubes.[2,9−11] Extensive research on fluoro-doped carbon materials, performed over the last 10 years, proved their unique electronic,[7,12] magnetic,[13,14] and luminescent[15,16] properties. Their high reactivity, thermal stability, and hydrophobic surface properties make these compounds an extraordinary material for applications in electrocatalysis, electrochemical sensing, spintronics, anticorrosion, separation processes, optoelectronics and photonics, and biomedicine.[8] In particular, the red-shift of the fluorescence emission frequency is of great interest for bioimaging applications because near-infrared light exhibits deeper tissue penetration.[17] The origin of the red-shifts, observed during fluorine doping of polyaromatic hydrocarbons dibenzoanthracene- and benzoperylene-type systems were explained by the electron-withdrawing character of fluorine.[18]

The stability of the C−F bond and the hydrophobic nature of the quantum carbon dots (QCD) make the synthesis of fluorinated quantum carbon dots (F-QCD) more challenging

Received: September 23, 2020
Revised: November 19, 2020
Published: December 16, 2020

ACS Publications

https://dx.doi.org/10.1021/acs.jpca.0c08694
J. Phys. Chem. A 2020, 124, 10954−10966

PCCP

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2019, 21, 9077

Excited states and excitonic interactions in prototypic polycyclic aromatic hydrocarbon dimers as models for graphitic interactions in carbon dots†

Baimei Shi,[a] Dana Nachtigallová,*[bc] Adélia J. A. Aquino,[a] Francisco B. C. Machado[d] and Hans Lischka*[a]

The study of electronically excited states of stacked polycyclic aromatic hydrocarbons (PAHs) is of great interest due to promising applications of these compounds as luminescent carbon nanomaterials such as graphene quantum dots (GQDs) and carbon dots (CDs). In this study, the excited states and excitonic interactions are described in detail based on four CD model dimer systems of pyrene, coronene, circum-1-pyrene and circum-1-coronene. Two multi-reference methods, DFT/MRCI and SC-NEVPT2, and two single-reference methods, ADC(2) and CAM-B3LYP, have been used for excited state calculations. The DFT/MRCI method has been used as a benchmark method to evaluate the performance of the other ones. All methods produce useful lists of excited states. However, an overestimation of excitation energies and an inverted ordering of states, especially concerning the bright HOMO–LUMO excitation, are observed. In the pyrene-based systems, the first bright state appears among the first four states, whereas the number of dark states is significantly larger for the coronene-based systems. Fluorescence emission properties are addressed by means of geometry optimization in the S_1 state. The inter sheet distances for the S_1 state decrease in comparison to the corresponding ground-state values. These reductions are largest for the pyrene dimer and decrease significantly for the larger dimers. Several minima have been determined on the S_1 energy surface for most of the dimers. The largest variability in emission energies is found for the pyrene dimer, whereas in the other cases a more regular behavior of the emission spectra is observed.

Received 31st January 2019,
Accepted 4th March 2019

DOI: 10.1039/c9cp00635d

rsc.li/pccp

1 Introduction

Excited state aggregates of polycyclic aromatic species, which are the building blocks of graphene quantum dots (GQDs) and carbon dots (CDs), are currently extensively studied systems as promising luminescent carbon nanomaterials[1] due to their potential applications in photonics and optoelectronics, organic devices, singlet fission processes, and bio- and medical applications.[2–7] Understanding and controlling the origin of the photoluminescence of GQDs and CDs, which can help in the rational design of carbon-based materials, was the subject of experimental and computational research (for recent studies see *e.g.* ref. 8–10). GQDs can be characterized as larger polycyclic aromatic hydrocarbons (PAHs), which obtain their discrete absorption and emission spectra due to their quantum confinement, as compared to graphene sheets.[11] CDs are more complex 3-dimensional systems which contain as important components graphitic regions responsible for their photoluminescence properties.[12] Due to the aggregation of PAHs in the graphitic regions of stacked sheets, the optical properties often resemble those of excimers (excited state dimers of two identical monomers) or exciplexes (excited state complexes of two non-identical monomers), complexes weakly associated in the ground state, but strongly interacting in the excited states.[13,14] Potential applications of these associates, including those in CDs, were already suggested in several studies[15–21] and their optical properties were investigated also computationally using model systems.[22–24]

The first experimentally observed pyrene excimer,[25] as one of the basic PAH excimer models, has received great attention

---

[a] *School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, P. R. China. E-mail: hans.lischka@univie.ac.at*

[b] *Institute of Organic Chemistry and Biochemistry v.v.i., The Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic. E-mail: dana.nachtigallova@marge.uochb.cas.cz*

[c] *Regional Centre of Advanced Technologies and Materials, Palacký University, 78371 Olomouc, Czech Republic*

[d] *Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos 12228-900, São Paulo, Brazil*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9cp00635d

THE JOURNAL OF
PHYSICAL CHEMISTRY
Letters

Letter

Cite This: *J. Phys. Chem. Lett.* 2019, 10, 5592−5597

pubs.acs.org/JPCL

Emission Energies and Stokes Shifts for Single Polycyclic Aromatic Hydrocarbon Sheets in Comparison to the Effect of Excimer Formation

Baimei Shi,[†] Dana Nachtigallová,[*,‡,§] Adélia J. A. Aquino,[†,∥] Francisco B. C. Machado,[⊥] and Hans Lischka[*,†,∥]

[†]School of Pharmaceutical Sciences and Technology, Tianjin University, Tianjin 300072, P. R. China

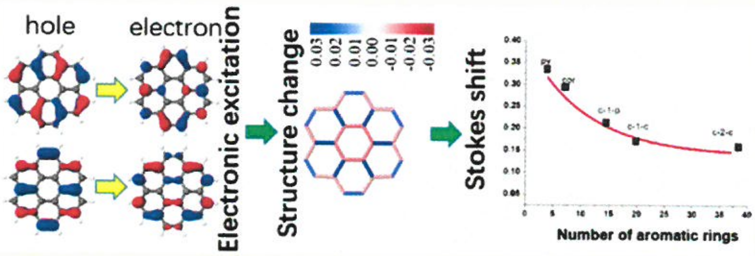
[‡]Institute of Organic Chemistry and Biochemistry v.v.i., The Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

[§]Regional Centre of Advanced Technologies and Materials, Palacký University, 78371 Olomouc, Czech Republic

[∥]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States

[⊥]Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos, 12228-900 São Paulo, Brazil

Supporting Information



ABSTRACT: Emission spectra of paradigmatic single-sheet polycyclic aromatic hydrocarbons (PAHs), pyrene, circum-1-pyrene, coronene, circum-1-coronene, and circum-2-coronene and Stokes shifts were computed and compared with previously calculated comparable data for relaxed excimer structures using the SOS-ADC(2), TD-B3LYP, and TD-CAM-B3LYP methods with multireference DFT/MRCI data as the benchmark. Vertical emission transitions and Stokes shifts were extrapolated to infinite PAH size. Comparison of Stokes shifts computed from theoretical monomer and dimer data confirms assumptions that relaxed excimers are responsible for the unusually large Stokes shifts in carbon dots observed in experimental investigations.

Polycyclic aromatic hydrocarbons (PAHs), conjugated aromatic molecules composed of fused benzenoid rings, have attracted attention as building units of carbon dot structures (CDs) which include graphene quantum dots (GQDs), composed of one or few graphene layers a few tens of nanometers in size, and carbon quantum dots (CQDs), possessing crystalline structure.[1] CDs are three-dimensional systems containing graphitic regions, which, in contrast to graphene, exhibit discrete absorption and emission spectra arising from their quantum confinement.[1,2] Because of their attractive photoluminescence properties and photostability, these materials find promising applications as photodetectors, solar cells, and light-emitting diodes.[3,4] The biocompatibility of CDs makes them ideal candidates for biosensors[5−8] and for bioimaging, drug delivery, and anticancer therapy.[9,10] However, despite their practical importance, major questions concerning the actual mechanisms of CD photoluminescence are still open,[1] especially the question of whether the fluorescence properties can be explained by single fluorophores or by aggregates.[11]

PAHs of various sizes have been used as model systems for studies on the luminescent behavior of CDs mentioned above.[1,12,13] Recently, Fu et al.[14] performed spectroscopic studies of model systems based on three PAHs, anthracene, pyrene, and perylene, embedded in a poly(methyl methacrylate) matrix to reproduce the features observed in actual CDs. An exciton self-trapping originating from relaxed excimer structures has been considered to be responsible for the large observed Stokes shifts. Even though these investigations point clearly to the important role of trapped excitons, a direct structural verification would be advantageous. The purpose of this work is to show, in combination with recent theoretical investigations of PAH dimers performed by our groupm[15] that these trapping effects induced by excimer formation indeed lead to significant Stokes shifts.

Inspired by the experimental observations of excitation-dependent photoluminescence, theoretical calculations, almost

Received: July 29, 2019
Accepted: September 3, 2019
Published: September 3, 2019

ACS Publications

DOI: 10.1021/acs.jpclett.9b02214
J. Phys. Chem. Lett. 2019, 10, 5592−5597