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Intersystem crossing at singlet conical intersections

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Abstract

The energy of the lowest triplet state of organic molecules is intermediate between the ground state and the first excited singlet. At the S_1/S_0 conical intersection, the two singlet states are degenerate. It is shown that for some molecules (ethylene, benzene, toluene and pyrrole) the T_1 state is also degenerate with the two singlet states. Moreover, the spin orbit coupling matrix element at this structure is necessarily large, so that intersystem crossing can be quite efficient. If the lowest triplet state is repulsive (as in the studied molecules) it may significantly contribute to the dissociation yield under certain experimental conditions.

Keywords: Intersystem crossing; Conical intersection; Pyrrole; Ethylene; Toluene; Photo-dissociation; Spinorbit coupling

1. Introduction

The factors affecting intersystem crossing (ISC) have been extensively discussed in the photochemical literature [1,2]. El-Sayed's rules [3] highlight the conservation of angular momentum and Salem and Rowland [4], assuming that the molecule has two completely localized radical-carrying orbitals with some p-character, they found that strong spinorbit coupling (SOC) is favored by three factors: (i) orthogonality of the axes of the two p-orbitals, (ii) "ionic" (zwitterionic, hole-pair) character in the singlet wave function, and (iii) spatial proximity of the two orbitals. Salem and Rowland's original paper treated biradicals, but their analysis can be applied to excited states as well. Salem's treatment, followed by Michl [5] emphasized the importance of excited zwitterion singlet states and the existence of certain geometries at which the two singlet states approach each other facilitating the non-radiative crossing between them. Actual crossing (a conical intersection ConInt) requires the use of two nuclear coordinates, and the consideration of two electron pairs. In standard organic photochemistry a four-electron system (tetra-radicaloid) is believed to often play a dominant role [6,7].

It is found that the nuclear distortions leading to the conical intersection often result in an increased zwitterionic character of the ground state wave function, raising its energy considerably. At the same time the energy of the purely covalent S_1 and T_1 states is increased to a smaller degree, and a conical intersection results. Moreover, the lowest triplet state lies usually at an energy intermediate between S_0 and S_1. At the S_0/S_1 conical intersection, the two states are degenerate so that the triplet is likely to lie at the same energy. In this communication, we show computationally that this is indeed the case for several systems. It is shown that the spin orbit coupling (SOC) matrix element, though much smaller than the vibronic coupling (VC) matrix element between the two singlet states, is large compared to its value at the minimum of the triplet and therefore intersystem crossing to the triplet is in principle possible at the conical intersection. This paper was motivated by recent experimental work in our group [8], in which the minor triplet channel was used to probe the efficiency of internal conversion, which in turn is believed to be mediated by a conical intersection. In this work it was shown that although the triplet is produced wit a small *quantum* yield ($\sim 10^{-5}$) it leads in the presence of O_2 to photo-oxidation, a reaction that dominates the *chemical* yield. Other possible photochemical consequences are discussed. Some of the conical intersections chosen for this paper have been extensively studied in the past and are well characterized.

2. Methodology and computational details

The location of minima, transition states and S_0/S_1 conical intersections was performed using the method previously described in detail [9]. State averaged calculations were used

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for the conical intersection. The energies of triplet states were calculated at selected geometries (stationary points) as well as at the geometry of the conical intersection. The CASSCF method as implemented in the GAMESS program suite [10] was used for the numerical evaluation of the structures and energies at these points. Spin-orbit coupling (SOC) calculations were performed with the CASSCF wave function and Pauli–Breit Hamiltonian including rigorous one and two-electron terms [11,12].

The choice of active space is discussed for the individual molecules. In general, we tried to keep roughly the same level of theory, using mostly a full π active space with all π electrons. The basis set used was cc-pVDZ.

3. Results and discussion

3.1. A general overview

Table 1 lists some of the main computational results of this work. Inspection of the table shows that in all molecules, a triplet state is very nearly degenerate with a singlet conical intersection. The SOC matrix element, calculated at this energy, is relatively large especially in the case of ethylene and pyrrole. By symmetry, ISC between states of the same orbital wave function are negligibly small. In the conical intersections discussed in this work, there is always a singlet of a different symmetry. This provides in principle a mechanism for the necessary spin flip.

In order to put the results in perspective, we compare them with the well-known case of benzene, for which the spin-orbit interaction has been extensively discussed as a prototype for aromatic compounds. Most studies considered the ISC process from the equilibrium position of the triplet state, which in benzene is $^3B_{1u}$. It was concluded [13–16] that the intersystem crossing rate constant for the transition T_1–S_0 in aromatic hydrocarbons is governed by first-order Herzberg–Teller spin-orbit coupling and not by non-adiabatic spin-orbit coupling. Both mechanisms are due to $\pi\sigma$ spin-orbit coupling induced by out-of-plane vibrations. The SOC matrix elements were found to be of the order of 0.3–0.6 cm^{-1}, leading to reasonably good agreement with experimental results. The SOC matrix element calculated for benzene at the ConInt is larger by an order of magnitude. We assign this change to the fact that in this case the two electronic states cross, increasing significantly the spin-orbit interaction. In order to estimate the change in ISC rate constant, at least two aspects have to be considered. In general, the intersystem rate constant may be written as:

$$k_{\mathrm{ISC(ST)}} = (2\pi h)^{-1}|V_{\mathrm{ST}}|^2 \cdot \mathrm{FC} \qquad (1)$$

V_{ST} is the SOC matrix element and FC is the Franck Condon factor. The rate constant is seen to be proportional to the square of the SOC matrix element. This factor is expected to lead to a 100-fold increase in k_{ISC}. In addition, most of the previous treatments utilized the Fermi Golden Rule approach and emphasized the role of the Franck–Condon factor, leading to the well-known deuteration enhancement effect on the phosphorescence of aromatic compounds. The energy gap between the T_1 and S_0 states required a substantial population of ground state vibrational levels, and the smaller number of CH stretch quanta compared to CD ones was found to explain the observed trend. At a crossing point, the rate constant is in general much larger, as no net electronic energy has to be partitioned to many vibrational quanta. Numerical values have to be calculated using quantum dynamics and are beyond the scope of this paper. However, it can be assumed that the T_1–S_0 ISC rate at the conical intersection is expected to be at least 100 times faster than in the equilibrium position of the triplet.

The structure and energy of the prefulvene-like ConInt were found to be very similar to those reported before [17,18] and are not reproduced here. As shown in ref. [17] the lowest triplet state in the Franck Condon region is the $^3B_{1u}$ one, but at the conical intersection geometry (C_s symmetry) it is the $1^3A''$ which correlates in D_{6h} symmetry with $^3B_{2u}$. The results of ref. [17] showed that the triplet is nearly degenerate with the S_0/S_1 ConInt, we find that they are actually degenerate [19]. This follows from the fact that the B_{2u} state (and the A'' one correlating with it) is essentially purely biradical [4], with minimal interaction between the two electrons that are unpaired in the triplet. Therefore, the singlet and triplet states are degenerate over the whole trajectory from the FC region to the conical intersection. The SOC matrix element calculated at the ConInt was 6.23 cm^{-1}, much larger than in the classical works which considered the triplet minimum [14–16].

3.2. Ethylene

The singlet conical intersection of ethylene is arguably one of the most extensively studied, mainly in connection with more complicated systems such as stilbene and retinal. In ethylene itself, photo-isomerization is not observed; rather several photo-dissociation pathways have been experimentally recorded. Recently several attempts to connect the calculated conical intersections with the observed dissociation channels have been made [20]. The photo-dissociation of ethylene following optical excitation is believed to occur on the grounds state potential surface following internal conversion (IC) via one or more conical intersections [21]. An ultrafast experiment

Table 1
Energies (absolute in Hartree and relative to S_0 minimum in eV) of some selected points on the potential energy surface of molecules studied (CASSCF/cc-pVDZ)

Molecule (active space)	S_0 (min)	T_1 (min)	$S_0/S_1/T_1$ at ConInt	SOC (cm^{-1})	$\mathrm{H}^\bullet + \mathrm{R}^\bullet$
Ethylene (12/11)	−78.16188	3.06(1^3A_2)	5.68 ($1^1A'/1^1A''/1^3A''$)	9.15 ($1^1A'/1^3A''$)	4.49($1^3A'$)
Pyrrole (6,6)	−208.88084	3.76(1^3B_2)	4.35 ($1^1A_1/1^1A_2/1^3A_2/1^3B_1$)	11.65 ($1^1A_1/1^3B_1$) 3.67 ($1^1A_1/1^3A_2$)	3.24(1^3A_2)
Toluene (8,7)	−269.83507	3.51 ($1^3A'$)	5.77 ($1^1A'/1^1A''/1^3A''$) 6.04 ($1^1A''/1^3A'/1^3A''$)	4.54 ($1^1A'/1^3A''$)	4.06($1^3A'$)

Spin orbit coupling (SOC) matrix elements at the ConInt geometries are also listed. In the last column the energy of the dissociated radical pair is listed.

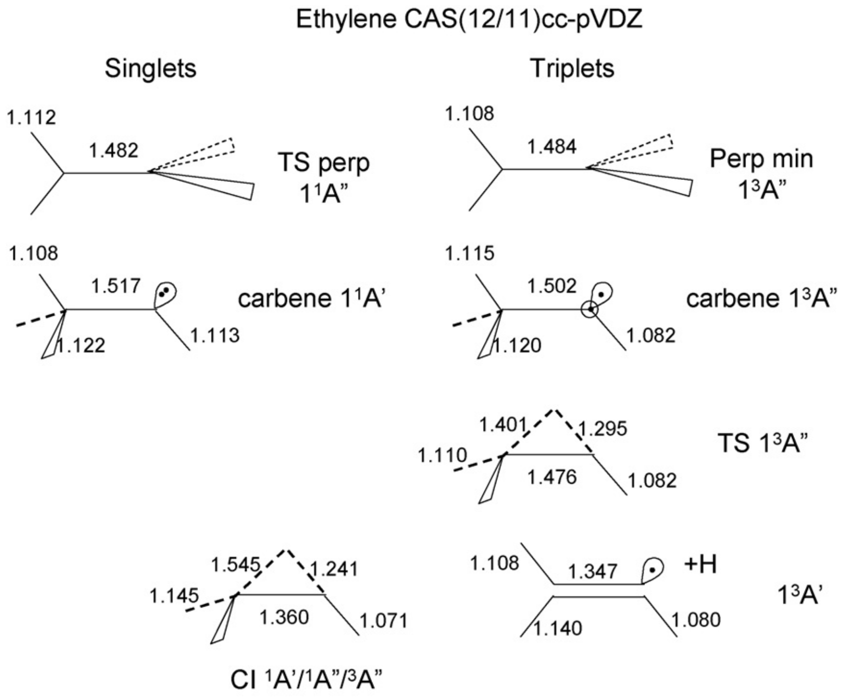

Fig. 1. The calculated structures of some species on the ethylene potential energy surface.

[22] reported a lifetime of 30 ± 10 fs for the S_1 state; the short lifetime was assigned to rapid IC followed by dissociation. The involvement of a triplet state has been usually neglected, assuming that intersystem crossing (ISC) is negligibly small compared to IC. Several recent high level calculations consider the singlet manifold only [23–26].

Our calculations show (Table 1), that the $(1^3A'')$ triplet state is indeed degenerate with the two singlet states at the H-atom migration conical intersection [27–29]. A transition to the triplet state might result in a lower ion yield due to a smaller photoionization cross-section. This might be one possible reason for the non-statistical nature of the dissociation process suggested by the calculations of ref. [26].

Fig. 1 shows schematically some of the structures relevant to this work calculated on the triplet and singlet surfaces (omitting Rydberg states which are not relevant for this discussion). Fig. 2 displays the calculated energy surface along the two coordinates leading to the conical intersection, highlighting the triplet state critical points. C_s symmetry was used throughout as the ConInt transforms in this symmetry group. Franck–Condon excitation leads to the $2^1A'$ state at about 7.7 eV (experimental value). This V state (Mulliken notation) tends to distort to a perpendicular biradical form of A'' symmetry (B_1 in D_{2d}). At its minimum, this species is a saddle point—a transition state between the two planar isomers of ethylene. The $1^1A'/1^1A''$ ConInt is reached by a combined motion along both the H migration coordinate and also the torsion coordinate leading to the carbene $(1^1A')$ minimum. As shown by the calculation, a $^3A''$ state is degenerate (within the computational error) with the $1^1A'/1^1A''$ ConInt at the geometry shown in Fig. 1. The energy of this ConInt (5.68 eV) is higher than the dissociation energy on the S_0 surface (4.49 eV), which is also the energy of the dissociated pair $(CH_2CH^\bullet + H^\bullet)$ triplet.

Lee and co-workers interpreted their molecular beam photodissociation data as occurring on the ground state surface. According to our results, some molecules have a chance to cross to the T_1 state, which is dissociative at any energy. In order to estimate the importance of this channel, dynamic calculations have to be carried out. The calculated SOC matrix element at the conical intersection is $11.65\,\mathrm{cm}^{-1}$, much smaller than the vibronic coupling which in similar systems was found to be an order of magnitude larger. In addition, the density of states on S_0 is much larger than on the T_1 surface, so that statistically the contribution of the triplet state is expected to be minor under

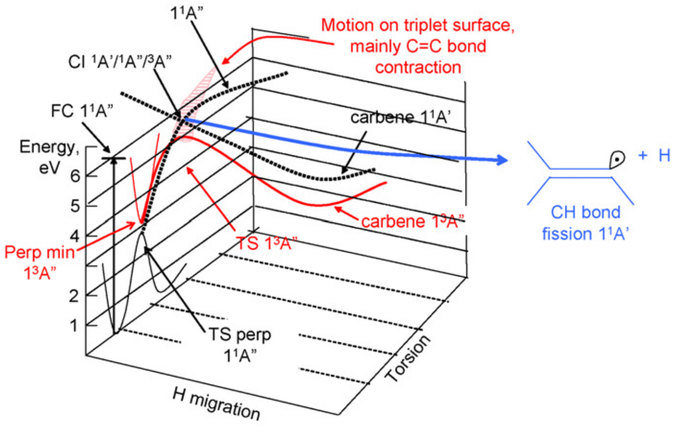

Fig. 2. A potential energy diagram showing triplet levels along the two coordinates leading to the conical intersection. In addition two coordinates are schematically highlighted: In pink, the transition from leading from the triplet transition state (TS) to the ConInt and a coordinate (leading to CH bond fission) from the ConInt. The dissociation can take place on the S_0 or T_1 surfaces. See Fig. 1 for the structures of the different species.

collision-free conditions. The situation may change when collisions are allowed: collisions may actually stabilize the ground state molecules by driving them to below the dissociation limit. In the case of the triplet, collisions will normally assist the dissociation. Thus, although the quantum yield of triplet molecules may be small, the chemical yield may be significant.

The possibility for crossing to the triplet at the conical intersection is built into the system, as shown in our calculations. The $^1A''$ and $^3A''$ states are almost degenerate at almost any position of the migrating H atom, as long as the electrons are largely occupying two orthogonal nearly degenerate MOs. However, the coupling between them is negligibly small due to symmetry. In contrast with the negligible SOC for two states of the same symmetry but different spins, the ConInt provides an opportunity for interaction between the lowest triplet and a singlet of different symmetry.

Caldwell et al. pointed out that for symmetry reasons the SOC matrix element vanishes at the perpendicular geometry [30]. Danovich et al. [31] emphasized the importance of pyramidalization for promoting ISC. Our numerical value is close to theirs, as we used the updated GAMESS program. It is clear that a similar treatment can be extended to larger ethylene derivatives, including cyclic ones in which torsion is limited [32].

3.3. Toluene

The lowest triplet state of toluene has been characterized in several solid state and gas phase environments. Haaland and Nieman [33] showed from the analysis of the vibronic structure of the phosphorescence spectrum that its structure is nearly C_{2V} and that it transforms as the B_1 irreducible representation. The molecule is distorted to a quinoidal ring (two short bonds and four long ones), with the methyl group lying at the apex of two long bonds and out of the plane of the ring. The non-planarity of the molecule reduces the symmetry to C_s symmetry, but the small out of plane angle (3.6°) allowed the analysis to be carried out in C_{2V}. The 0–0 band of the phosphorescence lies at 28994 cm^{-1} (3.59 eV), lower than the dissociation energy of the CH bond, as measured in the gas phase (3.89 eV) or of the CC bond (4.50 eV). However, since excitation of the first singlet–singlet band of toluene (the 1^1A_1–1^1B_2 transition) occurs at about 4.68 eV [34] the molecule has enough energy to dissociate, or to undergo other chemical transformations such as ring expansion to cycloheptatriene. As shown by Dietz et al. [35] the system transforms to the triplet state even under collision free conditions, upon excitation of the 0–0 band. The ISC yield is 0.64 and the intersystem crossing rate constant $8.5 \times 10^6\ \mathrm{s}^{-1}$. The fluorescence yield is 30% so that at this energy the internal conversion to the ground state is much slower (the IC yield is about 10 times smaller). This rather slow rate of ISC is strongly increased in the presence of heave gases in supersonic cooled clusters, reaching about $3 \times 10^8\ \mathrm{s}^{-1}$ in krypton clusters [36]. Even these rates are much smaller than IC rates expected at conical intersections.

Most kinetic data on the dissociation reaction were obtained in the gas phase upon excitation at 193 nm (6.4 eV). The main reaction is cleavage of one of the CH bonds of the methyl group and CH_3 elimination [37–43] but isotope scrambling experiments [44] showed that some molecules readily undergo isomerization to cycloheptatriene and re-aromatization prior to dissociation. The results have been analyzed in terms of reactions on the singlet state manifold, assuming that the dissociation is from vibrationally excited ground state molecules. The transition from the higher singlet states to S_0 are believed to involve conical intersections.

In our computations, the active space was seven orbitals with eight electrons: the orbitals were the six π orbitals (3 occupied and 3 unoccupied) and the occupied π pseudo orbital of the methyl group (i.e. eight electrons in seven orbitals). The structure of the calculated S_0/S_1 conical intersection is similar to that found for benzene [17,45]. The ground state potential curve ($1^1A'$ in C_s symmetry) crosses the S_1 state ($1^1A''$ in C_s symmetry). The minimum of the latter state, which is related to the 1^1B_{2u} state of benzene at 4.73 eV (calculated, 4.67 eV experimentally [34]) transforms through a low barrier to a prefulvene structure at which it is degenerate with the ground state. At this ConInt we found that a triplet state is also degenerate with the two singlet states; this is a $^3A''$ which at this point is T_1, but at the FC region was T_2. In fact the $1^1A''$ and $1^3A''$ states are degenerate along the entire coordinate leading from the minimum geometry to the prefulvene structure, which is, on the singlet surface, a transition state between two benzvalene isomers. On the triplet surface, the prefulvene structure is a minimum. The calculated structures of the species are shown in Fig. 3.

In contrast with case of benzene, there exists a low energy dissociation process to H atom plus benzyl radical; the required energy is much lower than that required for a CH bond cleavage in benzene due to the resonance stability of the benzyl radical. This is reaction takes place either on the S_0 surface or the T_1 one. This triplet state is of A' symmetry and is separated from the $T_1(A')$ minimum by a barrier. This triplet may be reached via the T_1/T_2 ($^3A'/^3A''$) ConInt (Fig. 3) which lies a little higher (0.3 eV) than the prefulvenic conical intersection which is also degenerate with the A'' triplet. Therefore, our results show that in the gas phase, an electronically excited toluene molecule may dissociate via the triplet state, in agreement with experimental data (especially when a heavy atom is adjacent to the molecule) [35].

The T_1/T_2 ConInt has an antiquinoid structure (Fig. 3) and is thus different from the prefulvene ConInt and also from the quinoid ConInt discussed in ref. [45] leading to Dewar benzene.

3.4. Pyrrole

The triplet states of pyrrole were observed by electron diffraction, yet no record of phosphorescence is known to us. High-level ab initio calculations were performed on the molecule [46–48], reaching very good agreement with experiment. The absorption spectrum in the 5.5–6.5 eV region was found to include several valence and Rydberg states, with the intensity due mainly to ππ* and Rydberg states. As the NH bond is lengthened these states are coupled to πσ* states, which become the lowest energy ones near the dissociation limit (experimental value 4.07 eV [49]). It was found that the NH bond dissociation occurs adiabatically, and that the pyrrolyl radical acts as a spectator to the NH bond

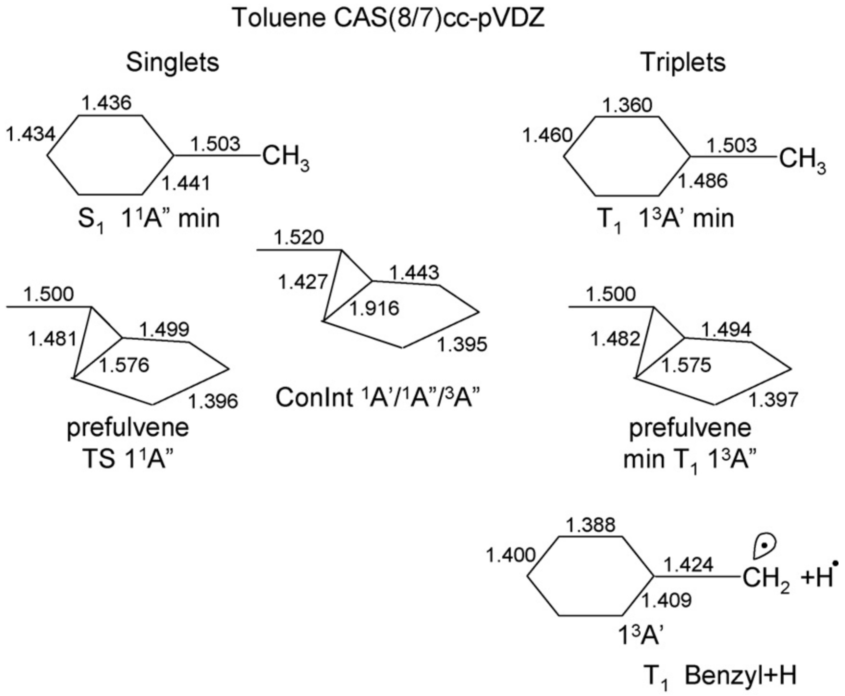

Fig. 3. The calculated structures of some species on the toluene potential energy surface. The $^3A'/^3A''$ ConInt is a triplet degeneracy (T_1/T_2).

Table 2
Structures and relative energies of some pyrrole states, CASSCF(6,6)/cc-pVDZ

State	NH	NC_2	C_2C_3	C_3C_4	Energy (eV)
1^1A_1	0.995	1.368	1.375	1.430	0
Exp [53]	0.996	1.370	1.382	1.417	0
1^3B_2 min	0.991	1.415	1.475	1.355	4.03
ConInt: $1^1A_1/1^1A_2/1^3A_2/1^3B_1$	1.715	1.374	1.391	1.459	4.34
1^3A_2 Diss		1.338	1.466	1.359	3.24
1^3B_1 Diss		1.386	1.366	1.492	3.70

dissociation process [50]. This means that the excess energy available in the molecule is not redistributed statistically, as expected from standard theories of chemical reaction (RRKM), but goes selectively to the NH bond dissociation energy, as predicted by Sobolewski et al. [51].

Since we were interested mostly in the triplet states, we used a modest (6,6) active space (five π orbitals plus the σ^*_{NH} antibonding orbital). The structures obtained are summarized in Table 2 and Fig. 4 shows schematically the shapes of the pyrrolyl radicals of A_2 and B_1 symmetry calculated at the dissociation limit. It is seen that for the ground state excellent agreement with experimental results [52] are obtained.

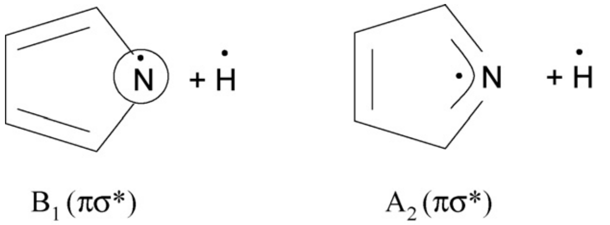

Fig. 4. The calculated structures of the A_2 and B_1 states of pyrrole at the dissociation limit.

Fig. 5 displays the calculated energy level diagram along the NH distance.

As seen from Fig. 5, the two spin components of the states $1A_2$ and $1B_1$ are nearly degenerate along the R_{NH} coordinate. This follows from the fact that the two electrons occupy two non-interacting orbitals. The absorption spectrum of pyrrole in the 5–6 eV range is complex, but the strongest transition is to the $1^1B_2(\pi\pi^*)$ state, which crosses over to one or both $\pi\sigma^*$ states.

Neither fluorescence nor phosphorescence was reported for pyrrole. Fluorescence was observed for the *N*-methyl derivative [55]; its excitation spectrum was very narrow and was assigned to the 1^1A_2(3s) Rydberg state. At higher energies on the onset of valence states an efficient radiationless channel was opened, eliminating the fluorescence. The absence of fluorescence was

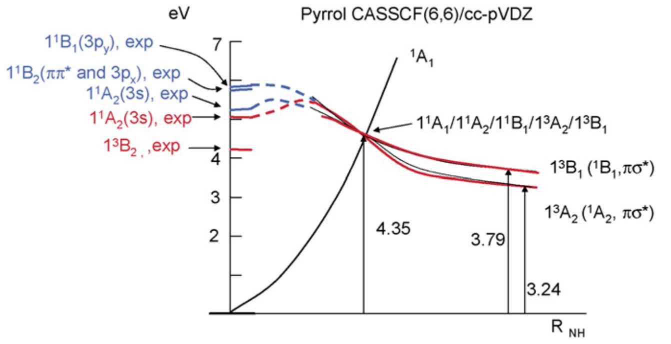

Fig. 5. A partial energy level diagram for pyrrole based on the calculations of this work. The Franck–Condon energies were not calculated, and were taken from the experimental work of ref. [54] as interpreted in ref. [47] (Rydberg states excluded).

assigned to the coupling between the initially excited state ($\pi\pi^*$) and dissociative $\pi\sigma^*$ states leading to cleavage of the N–H bond [51]. The crossing between the states is an ultrafast process taking place through a conical intersection at an estimated 30 fs time period [56]. It was assumed that the dissociation takes place on the singlet manifold, as the transition to the triplet was considered to be on a much slower time scale. Picosecond intersystem crossing (ISC) is known in the case of another aza-aromatic, pyridine [57,58]. This rapid ISC is assigned to the strong coupling between the $n\pi^*$ singlet and the close-lying $\pi\pi^*$ triplet according to El Sayed's rules [3]. In the case of pyrrole, the reasoning underlying the El Sayed rules (conservation of angular momentum during intersystem crossing) applies for the two states A_2 and B_1.

As an aside we note that the triply degenerate singlet state found for pyrrole may be connected with the fact that the pyrrolyl radical is a quasi Jahn–Teller system having 5π electrons in a five membered ring. The general case of higher degeneracy was discussed by us some time ago [59], this appears to be another example of the general case.

4. Conclusion

The transition to the triplet states when internal conversion is rapid has been in general neglected. As shown here situations may arise in which the triplet is populated and may contribute to the observed dynamics. Dissociation reactions are of particular interest in this context as triplet states are often dissociative. Examples are already available in the literature, primarily when heavy atoms are involved, but also in phenyl derivatives such as ethylbenzene and *para*-fluoroethylbenzene [60].

Acknowledgments

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References

[1] S.P. McGlynn, T. Azumi, M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice-Hall, Englewood-Cliffs, NJ, 1969.

[2] M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH, New York, 1995.

[3] M.A. El Sayed, J. Chem. Phys. 38 (1963) 2834–2838.

[4] L. Salem, C. Rowland, Angew. Chem. -Int. Ed. 11 (1972) 92–111.

[5] J. Michl, J. Am. Chem. Soc. 118 (1966) 3568–3579.

[6] M. Olivucci, I.N. Ragazos, F. Bernardi, M.A. Robb, J. Am. Chem. Soc. 115 (1993) 3710–3721.

[7] S. Zilberg, Y. Haas, Chem. Eur. J. 5 (1999) 1755–1765.

[8] S. Cogan, Y. Haas, S. Zilberg, Photo-oxidation of indenylidene-dihydropyridine derivatives: conical intersection manipulation by solvent polarity. Paper PHYS-394, Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, September 10–14, 2006.

[9] S. Zilberg, Y. Haas, PCCP 4 (2002) 34–42.

[10] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347–1363.

[11] D.G. Fedorov, M.S. Gordon, J. Chem. Phys. 112 (2000) 5611–5623.

[12] D.G. Fedorov, S. Koseki, M.W. Schmidt, M.S. Gordon, Int. Rev. Phys. Chem. 22 (2003) 551–592.

[13] D.S. McClure, J. Chem. Phys. 20 (1952) 682–686.

[14] H.F. Hameka, L.J. Oosterfoff, Mol. Phys. 1 (1958) 358–371.

[15] B.R. Henry, W. Siebrand, J. Chem. Phys. 54 (1971) 1072–1085.

[16] F. Metz, S. Friedrich, C. Hohlneicher, Chem. Phys. Lett. 16 (1972) 353–358.

[17] A. Sobolewski, C. Woywod, W. Domcke, J. Chem. Phys. 98 (1993) 5627–5641.

[18] A. Toniolo, A.L. Thompson, T.J. Martınez, Chem. Phys. 304 (2004) 133–145.

[19] At the CASSCF(8,7)/DZV level of theory, the following energies (Hartree units) were obtained: S_1/S_0: −230.51332/−230.51296 (State average −230.50813); T_1 at the same geometry −230.51564. The *S*/*T* energy difference is about 1 kcal/mol. By comparison, the optimized energies of the prefulvene singlet and triplet minima differed by about 3 kcal/mol (triplet more stable).

[20] M. Barbatti, J. Paier, H. Lischka, J. Chem. Phys. 121 (2005) 11614.

[21] A.B. Balko, J. Chang, Y.T. Lee, J. Chem. Phys. 97 (1992) 935–942.

[22] P. Farmanara, V. Stert, W. Radloff, Chem. Phys. Lett. 288 (1998) 518–522.

[23] M. Barbatti, M. Ruckenbauer, H. Lischka, J. Chem. Phys. 122 (2005) 174307.

[24] J.J. Lin, C.C. Wang, Y.T. Lee, X. Yang, J. Chem. Phys. 113 (2000) 9668–9677.

[25] A.H.H. Chang, A.M. Mebel, X.-M. Yang, S.H. Lin, Y.T. Lee, J. Chem. Phys. 109 (1998) 2748–2761.

[26] A.H.H. Chang, D.W. Hwang, X.-M. Yang, A.M. Mebel, S.H. Lin, Y.T. Lee, J. Chem. Phys. 110 (1999) 10810–10820.

[27] I. Ohmine, J. Chem. Phys. 83 (1985) 2348–2362.

[28] M. Ben-Nun, T.J. Martınez, Chem. Phys. 259 (2000) 237–248.

[29] R.P. Krawczyk, A. Viel, U. Manthe, W. Domcke, J. Chem. Phys. 119 (2003) 1397–1411.

[30] R.A. Caldwell, L. Carlacci, C.E. Doubleday, T.R. Furlani, H.F. King, H.J.W. McIver, J. Am. Chem. Soc. 110 (1988) 6901–6902.

[31] D. Danovich, C.M. Marian, T. Neuheuser, S.D. Peyerimhoff, S. Shaik, J. Phys. Chem. A 102 (1998) 5923–5936.

[32] M. Woeller, S. Grimme, S.D. Peyerimhoff, D. Danovich, M. Filatov, S. Shaik, J. Phys. Chem. A 104 (2000) 5366–5373.

[33] D.M. Haaland, G.C. Nieman, J. Chem. Phys. 59 (1973) 4435–4457.

[34] J.B. Hopkins, D.E. Powers, R.E. Smalley, J. Chem. Phys. 72 (1980) 5039–5048.

[35] T.G. Dietz, M.A. Duncan, R.E. Smalley, J. Chem. Phys. 76 (1982) 1227–1232.

[36] R.J. Doyle, E.S.J. Love, R. Da Campo, S.R. Mackenzie, J. Chem. Phys. 122 (2005) 194315.

[37] H. Hippler, V. Schubert, J. Troe, H.J. Wendelken, Chem. Phys. Lett. 84 (1981) 253–256.

[38] J. Park, R. Bersohn, I. Oref, J. Chem. Phys. 93 (1990) 5700–5708.

[39] R. Fröchtenicht, J. Chem. Phys. 102 (1994) 4850–4859.

[40] N. Nakashima, K. Yoshihara, J. Phys. Chem. 93 (1989) 7763–7771.

[41] K. Luther, J. Troe, K.L. Weitzel, J. Phys. Chem. 94 (1990) 6316–6320.

[42] U. Brand, H. Hippler, L. Lindemann, J. Troe, J. Phys. Chem. 94 (1990) 6305–6316.

[43] T. Shimada, Y. Ojima, N. Nakashima, Y. Izawa, C. Yamanaka, J. Phys. Chem. 96 (1992) 6298–6302.

[44] C.-K. Lin, C.-L. Huang, J.-C. Jiang, A.H.H. Chang, Y.T. Lee, S.H. Lin, C.-K. Ni, J. Am. Chem. Soc. 124 (2002) 4068–4075.

[45] I.J. Palmer, I.N. Ragazos, F. Bernardi, M. Olivucci, M.A. Robb, J. Am. Chem. Soc. 115 (1993) 673–682.

[46] L. Serrano-Andres, M. Merchan, I. Nebot-Gil, B.O. ROOS, M. Fülscher, J. Am. Chem. Soc. 115 (1993) 6184–6197.

[47] B.O. Roos, P.-A. Malmqvist, V. Molina, L. Serrano-Andres, M. Merchan, J. Chem. Phys. 116 (2002) 7526–7536.

[48] V. Vallet, Z. Lan, S. Mahapatra, A.L. Sobolewski, W. Domcke, Faraday Dis. 127 (2004) 283–293.

[49] B. Cronin, A.L. Devine, M.G.D. Nix, M.N.R. Ashfold, Phys. Chem. Chem. Phys. 8 (2006) 3440–3445.

[50] M.N.R. Ashfold, B. Cronin, A.L. Devine, R.N. Dixon, M.G.D. Nix, Science 312 (2006) 1637–1640.

[51] A.L. Sobolewski, W. Domcke, C. Dedonder-Lardeux, C. Jouvet, Phys. Chem. Chem. Phys. 4 (2002) 1093–1100.

[52] L. Nygaard, J.T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, G.O. Sorensen, J. Mol. Struct. 3 (1969) 491–506.

[53] L. Nygaard, J.T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, G.O. Sorensen, J. Mol. Struct. 3 (1969) 491.

[54] M.H. Palmer, I.C. Walker, M.F. Guest, Chem. Phys. 238 (1998) 179–199.

[55] R. McDiarmid, X. Xing, J. Chem. Phys. 105 (1996) 867–873.

[56] H. Köppel, E.V. Gromov, A.B. Trofimov, Chem. Phys. 304 (2004) 35–49.

[57] I. Yamazaki, K. Sushida, H. Baba, J. Chem. Phys. 71 (1979) 381–387.

[58] M. Chachisvilis, A.H. Zewail, J. Phys. Chem. A 103 (1999) 7408–7418.

[59] S. Zilberg, Y. Haas, J. Am. Chem. Soc. 125 (2003) 1810–1820;
S. Zilberg, Y. Haas, J. Phys. Chem. A 107 (2003) 1222–1227.

[60] C.-L. Huang, Y.A. Dyakov, S.H. Lin, Y.T. Lee, C.-K. Ni, J. Phys. Chem. A 109 (2005) 4995–4999.