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A theoretical study of singlet low-energy excited states of the benzene dimer

Tomás Rocha-Rinza [a,b], Luca De Vico [a], Valera Veryazov [a], Björn O. Roos [a,*]

[a] *Department of Theoretical Chemistry, Chemical Centre, P. O. Box 124, S-221 00 Lund, Sweden*
[b] *Departamento de Física y Química Teórica, Facultad de Química, Universidad Nacional Autónoma de México, Circuito Escolar. Ciudad Universitaria, 04510 México D. F. México*

Abstract

The singlet ground and low-energy excited states of the benzene dimer in D_{6h} geometry are characterized using second order multireference perturbation theory (CASPT2). The counterpoise-corrected spectroscopic parameters of the benzene excimer are in quantitative agreement with experiment. The same method was used to compute a submanifold of the potential energy hypersurface of the first excited state of the benzene dimer, exhibiting two local minima in addition to a saddle point between them. This study demonstrates the suitability of CASPT2 to describe the benzene excimer and suggests that the method can be used to describe weak intermolecular interactions involving excited states.
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1. Introduction

Aromatic excimers, AE, are dimeric species that are stable only in an excited electronic state. They play a pivotal role in several photochemical processes including photodimerization and photolysis in rigid matrices [1]. The analysis of AE fluorescence has several applications. For instance, in material science it is used to study interactions within polymer materials [2] and to monitor processes carried out during photoinitiated polymerization [3]. In qualitative and quantitative analysis, it has been applied to quantify putrescine and cadaverine in seafood [4], and to identify electron-deficient molecules, giving it a potential use to detect explosives containing nitro-compounds [5]. In combustion science there is evidence that AE fluorescence in flames indicates aggregation of polycyclic aromatic hydrocarbons, which is an important step in soot formation [6].

These applications have motivated both experimental and theoretical studies aimed at understanding both spectroscopy and structure of AE. A major part of the knowledge about AE comes from spectroscopic measurements in the condensed phase, mainly in solution and the crystalline state [7] but also in adsorbates [8] and dispersed microcrystals [9]. In these studies, the appearance of a structureless, concentration-dependent and red-shifted fluorescence band is characteristic of an excimer [7]. More recently, the dynamics of formation of AE [10] and the nature, bound or repulsive, of the corresponding potential energy surfaces [11] can be investigated by spectroscopy of expanded supersonic jets using pump–probe techniques. Almost all computational studies on AE have been carried out using semi-empirical and singles configuration interaction, CIS, methodologies [12–15] in spite of the insufficiencies of these methods in describing excited states [16,17] and weak intermolecular interactions. Despite the sometimes questionable behaviour of time-dependent density functional theory, TDDFT, in calculations of excitation energies [16] Amicangelo's results are in reasonable agreement with experiment for several spectroscopic parameters of the benzene excimer, BE [18].

The excited states of aromatic molecules have near degeneracies in the π electron system [17] and the dynamic

electron correlation is fundamental for both the calculation of transition energies [16] and the description of weak van der Waals interactions [19]. The multireference perturbative method CASPT2 [20] takes into account these correlation effects, and has been successfully applied in studies of the electronic spectra of a large number of aromatic molecules [21]. The suitability of CASPT2 to study excited states of aromatic molecules makes it potentially useful for the description of AE. In the present contribution, we investigate this by characterizing the potential energy curves of the benzene dimer, BD, in its ground state, A_{1g}, and the singlet low-energy excited states B_{2u}, E_{1u} and E_{1g} in D_{6h} geometry. In addition, one submanifold of the potential energy hypersurface for the lowest A'' state of BD in a C_s geometry was computed in order to investigate the experimentally observed process [10]

$$(C_6H_6)_2^\star \rightarrow (C_6H_6)_2^\star$$
$$\text{excited} \qquad \text{benzene}$$
$$\text{T-shaped} \qquad \text{excimer} \qquad\qquad (1)$$

The results demonstrate the adequacy of the CASPT2 method to describe the lowest excited states of BD and they lend support to the idea that this approach can be used to investigate intermolecular interactions in the excited state.

2. Computational details

All calculations were carried out by using the Molcas 6.2 system [22] and an Atomic Natural Orbital, ANO, basis set with the contraction scheme (C,4s3p2d/H,3s2p). This orbital basis was chosen since ANO basis sets are known to be most suitable for the study of different regions of the electronic spectrum [16] and their use with the CASPT2 provides accurate results for the transition energies of the benzene molecule [17]. The newly developed IPEA modification of the zeroth order Hamiltonian was used throughout [23]. The active space comprised the six π valence orbitals of both benzene molecules and twelve electrons. The geometry of both monomers was fixed to the experiment [24] in all calculations. This approximation is reasonable because a full geometry optimization at the described level of theory of BE within the D_{6h} geometry did not substantially change the geometry of the monomers. The used degrees of freedom are shown in Fig. 1. For the potential energy curves in D_{6h} geometry, the distance between the monomers was varied from 2.7 to 9.5 Å in increments ranging from 0.04 to 1 Å. The grid for the potential energy surface involved changes in R and θ of 0.2 Å and 5° respectively, while the minima and the saddle point were searched by varying $R = 0.1$ Å and $\theta = 1°$ in the vicinity of these points. The importance of Basis Set Superposition Error, BSSE, in the study of weak intermolecular interactions is well-known [25], and it was taken into account by the counterpoise method, CP [26]. For this purpose, the energies of a benzene molecule in the lowest B_{2u} and E_{1u} states were calculated in presence of ghost orbitals, in
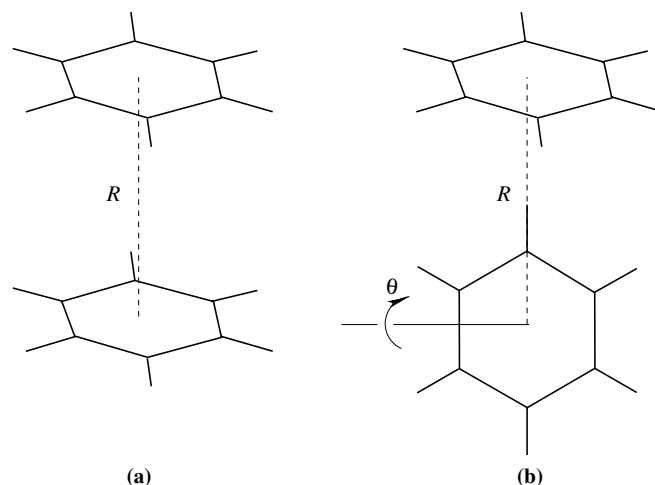

Fig. 1. Degrees of freedom for (a) the potential energy curves for the lowest A_{1g}, B_{1g}, B_{2u}, E_{1g} and E_{1u} singlet states of the benzene dimer in D_{6h} geometry and (b) the potential energy surface of A'' of the benzene dimer in C_s geometry. The values $\theta = 0°$ and $\theta = 90°$ correspond to a D_{6h} and a C_{2v} T-shaped geometries respectively.

consistency with the fact that an excimer is formed due to the attractive interaction between a molecule in an excited state and another in ground state. By referring the energy of all species to the energy of two ground-state monomers at infinite separation, the CP-corrected energy of an excited state $(C_6H_6)_2^\star$ of BD is

$$E(CP) = E^{\alpha \cup \beta}\left[(C_6H_6)_2^\star\right] - \left\{E^{\alpha \cup \beta}\left[C_6H_6^\star\right] + E^{\alpha \cup \beta}\left[C_6H_6\right]\right\} + E^{\alpha}\left[C_6H_6^\star\right] - E^{\alpha}\left[C_6H_6\right]$$

In this equation $(C_6H_6)_2^\star$ results from the interaction of $C_6H_6^\star$ with C_6H_6 and Xantheas notation [27] is used throughout: $E^{\sigma}[A]$ stands for the energy of species A using basis set σ. This procedure is equivalent to the one used by Pecul et al. in their study of excited states of Be_2 [28]. In virtue of the non-equivalence of the monomers in the potential energy surface, it is necessary to consider two cases for CP correction, each corresponding to either the top or the stem of the T-shaped dimer being in the first excited state.

3. Results and discussion

3.1. Potential energy curves for ground and low energy excited states of BD in D_{6h} geometry

The potential energy curves for the parallel BD in the ground state, A_{1g}, and low-energy excited states B_{1g}, B_{2u}, E_{1u}, and E_{1g} are presented in Fig. 2. Since the nature of the ground state is not multiconfigurational, CASPT2 results for A_{1g} are similar to those found with MP2 approximation reported elsewhere [33]. For the excited states curves, it is observed that the interaction of a ground state benzene molecule with an excited B_{2u} gives rise to two excited states of BD belonging to the representations B_{1u}
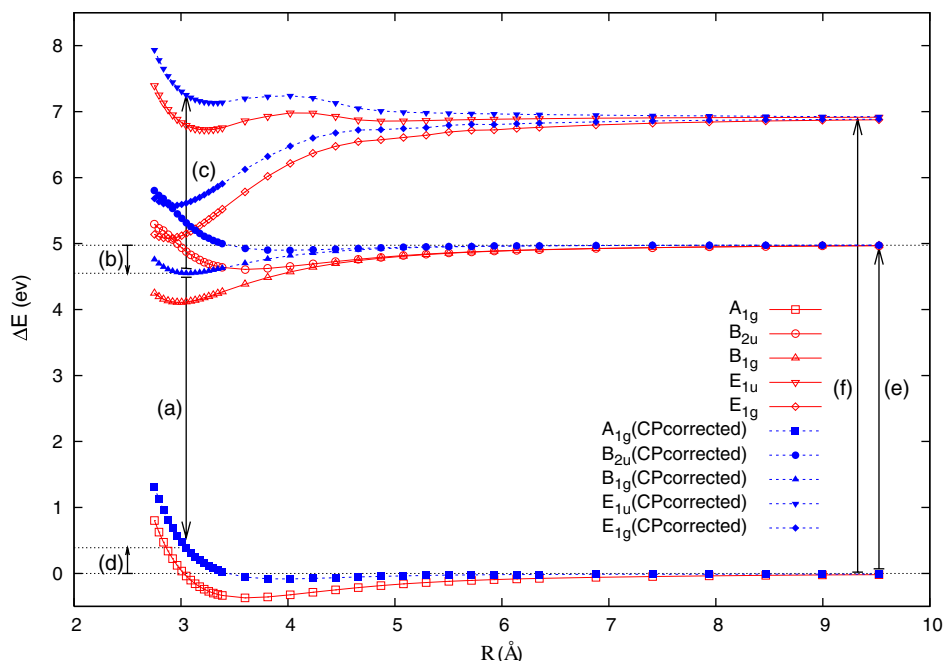
Fig. 2. Potential energy curves for the ground and some low energy excited states of the benzene dimer. The parameters used for comparison between theory and experiment are (a) emission, (b) binding, (c) absorption and (d) repulsion energy of the benzene excimer, in addition to (e) $^1A_{1g} \rightarrow {}^1B_{2u}$ and (f) $^1A_{1g} \rightarrow {}^1E_{1u}$ monomer absorption energies.

and B_{1g}. In the long range limit where benzene molecules do not interact with each other, the Hamiltonian of the total system is just the sum of the Hamiltonians of the isolated units and the wavefunction is

$$\Psi = \Psi_1^{A_{1g}} \Psi_2^{B_{2u}} \qquad (2)$$

where the subindex and superindex refer to the number of the molecule and the electronic state respectively. In Eq. (2), there is no need to antisymmetrize with respect to the interchange of electrons in different molecules since they are not interacting, and moreover they are distinguishable, since they are in different electronic states. This implies that even though the point group of the nuclear framework is D_{6h}, the wavefunction (2) does not belong to any irreducible representation of this point group, but rather to the B_2 representation of C_{6v}. As soon as both molecules interact, they become undistinguishable and the wavefunction belongs to an irreducible representation of the point group $D_{6h} = C_{6v} \otimes C_s$. Hence, the possible states for BD are given by the direct product of the representation B_2 with the irreducible representations of the C_s point group, that is B_{2u} and B_{1g} of D_{6h} with

$$\Psi^{B_{1g}} \approx \Psi_1^{A_{1g}} \Psi_2^{B_{2u}} - \Psi_1^{B_{2u}} \Psi_2^{A_{1g}} \qquad (3)$$

$$\Psi^{B_{2u}} \approx \Psi_1^{A_{1g}} \Psi_2^{B_{2u}} + \Psi_1^{B_{2u}} \Psi_2^{A_{1g}} \qquad (4)$$

Antisymmetry is implicit in these equations. Similar considerations follow for the interaction of E_{1u} and A_{1g} molecules giving rise to E_{1g} and E_{1u} states of BD. The interaction between a B_{1u} and A_{1g} molecules would give rise to B_{1u} and B_{2g} states of BD. Neither of these states

has been observed. This is why the $^1A_{1g} \rightarrow {}^1B_{1u}$ monomer transition is not considered in the present study. The CASPT2 approximation predicts a crossing of the E_{1g} and B_{2u} states and that the states B_{1g}, E_{1g} and E_{1u} have local minima, while all these states but E_{1g} are repulsive at the CASSCF level of theory (curves not shown). This evidences the importance of dynamic correlation in the interaction between the monomers comprising BE and other low-energy excited states of BD. Correlation is important also in the calculation of excitation energies as has been pointed out in the benzene monomer [17]. This has important consequences in the study of the spectrum of the BE. For example the CASSCF excitation energy for the monomer transition $A_{1g} \rightarrow B_{2u}$ is in good agreement with experiment while the transition $A_{1g} \rightarrow E_{1u}$ is too high [17]. This makes the BE absorption energy[1] $B_{1g} \rightarrow E_{1u}$ be overestimated (4.70 eV) as well. The lacking of a minimum in the B_{1g} state and the omission of dispersive forces by CASSCF have as consequences that the BE emission energy $B_{1g} \rightarrow A_{1g}$ and the repulsion energy of the BE are also overrated: 4.46 eV and 0.95 eV. (See Table 1 for the experimental values).

The depth of the CASPT2 local minima is drastically reduced by the CP correction, which is necessary in order to get results in agreement with experiment, specially for the binding energy of BE. The CP correction affects in a different magnitude the considered electronic states, A_{1g}

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[1] Calculated at the BE geometry predicted by CASPT2, since the CASSCF B_{1g} curve is repulsive.

Table 1
Comparison between CASPT2 and experimental values (in eV) for selected spectroscopic parameters of the benzene excimer

Parameters	CASPT2	CASPT2 (CP-corrected)	TDDFT [18]	Experimental
(a) Emission energy ($B_{1g} \rightarrow A_{1g}$)	3.99	4.16	4.29	3.94 [29]
(b) Binding energy	0.86	0.43	0.46	0.34–0.36 [30,31]
(c) Absorption energy ($B_{1g} \rightarrow E_{1u}$)	2.80	2.70	–	2.48 [10]
(d) Repulsion energy	0.12	0.39	0.63	0.42 [31]
(e) $^1A_{1g} \rightarrow {}^1B_{2u}$ monomer absorption energy	4.98	4.98	5.40	4.90 [32]
(f) $^1A_{1g} \rightarrow {}^1E_{1u}$ monomer absorption energy	6.92	6.92	–	6.96 [32]

having the smallest correction while the states B_{1g} and E_{1g} have the largest BSSE in the region around the excimer. This reveals the importance of BSSE in the description of the spectrum of BE. In Table 1, a comparison between experimental and theoretical values for the parameters highlighted in Fig. 2 is presented. It is noted that all the CP-corrected values are in good agreement with experiment and all of them are improved with respect to TDDFT [18].

In order to get further insight of the importance of BSSE in the study of the spectrum of the BE, the effect of increasing and decreasing the basis set in the local minimum of B_{1g} was investigated. The CP-corrected binding energies predicted with the (C,3s2p1d/H,2s1p) and (C,4s3p2d1f/H,3s2p1d) ANO basis sets are 0.36 and 0.51 eV while the BSSE are 0.60 and 0.28 eV respectively. These values were calculated at the geometry of the BE found with the use of the contraction scheme (C,4s3p2d/H,3s2p). The relative magnitudes of BSSE are those expected with respect to the size of the basis set. The addi-

tion of f and d functions centered on the carbon and hydrogen atoms respectively does not change in a significant manner (< 0.1 eV) the values shown in Table 1. The local minima for B_{1g}, E_{1g} and E_{1u} are located at 3.05, 2.92 and 3.30 Å respectively, for the CP-corrected curves. The first of these values is smaller than the one obtained by TDDFT (3.15 Å) and both are in accordance with the experimental evidence based in volume contractions and excimer fluorescence from crystalline structures suggesting that the distance between rings of AE is in the range 3–3.5 Å [7]. The curves in Fig. 2 constitute further evidence for the arguments used to explain BE fluorescence: after one molecule is excited into the first excited state, it can interact attractively with another molecule in the ground state reducing the energy of the system, [18,34] while the red-shifted and structureless fluorescence of the excimer with respect to the monomer is accounted by the excimer's equilibrium structure corresponding to a repulsive portion of the ground state potential energy curve ((a) in Fig. 2).
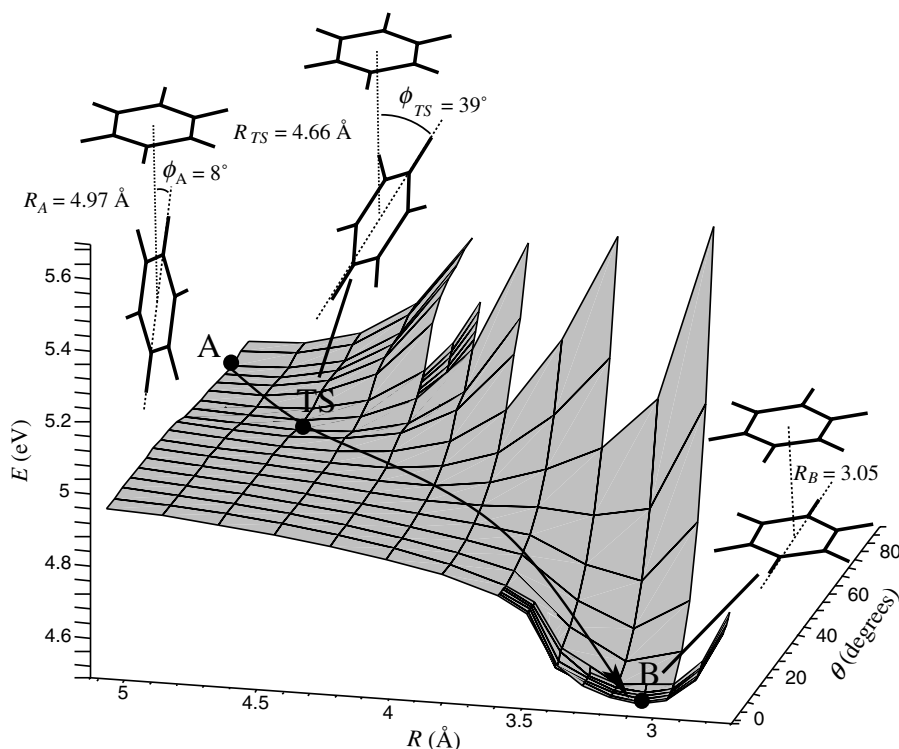

Fig. 3. Counterpoise-corrected potential energy surface. Points A, B and TS correspond to a tilted excited T-shaped benzene dimer, the benzene excimer and the transition state between them while ϕ is the complementary angle of θ.

3.2. Potential energy surface for A″ state

Given the suitability of the CASPT2 method with the ANO basis set and the chosen active space in the calculation of the spectroscopic parameters of BE described in Subsection 3.1, this methodology was used to describe a submanifold of the potential energy hypersurface corresponding to the lowest A″ state of BD. Both CP corrections (end of Section 2) were applied in the whole surface, resulting two surfaces very similar both qualitatively and quantitatively regarding their topological features. The surface in which the CP correction is applied considering the stem in the excited state is presented in Fig. 3. For the uncorrected and both CP-corrected surfaces, the absolute minimum in energy is found to belong to the D_{6h} point group but changes in θ until 5° destabilize the system only very slightly as already predicted by TDDFT [18]. In fact, changes in the distance between the two monomers affect far more strongly the energy than changes in θ. This minimum corresponds to the BE. The results for both CP corrections near the BE equilibrium energy are almost identical due to the near equivalence of both monomers around this point. There is another far more shallow local minimum in the surface corresponding to a tilted T-shaped excited state with $R = 4.97$ Å and $\theta = 82.0°$. Between these two minima there is a saddle point, at $R = 4.66$ Å and $\theta = 51°$ in both corrected surfaces. The activation energy for the conversion of the excited T-shaped BD into the BE is 0.02 eV for the CP corrected surfaces, which is lower than the experimental value 0.11 eV [35]. Given that there are two sources of gradient trajectories in the potential energy surface and a sink for two trajectories starting at these sources, it is possible to schematize a qualitative reaction path for process (1) as presented in Fig. 3.

4. Concluding remarks

The multireference perturbative method CASPT2 was used to characterize the ground and low-energy excited states of BD in D_{6h} geometry. The spectroscopical parameters calculated from CP-corrected curves are in quantitative agreement with experiment. A submanifold of the potential energy surface of the A″ state was also described, and is shown to exhibit two local minima corresponding to BE and a tilted excited T-shaped BD as well as a saddle point between them.

Acknowledgements

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