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Absorption and resonance Raman study of the pyromellitic diahydride anion via density functional theory

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Abstract

The electronic structure of the low-energy states of the pyromellitic diahydride (PMDA) anion is investigated in terms of the VWN (Vosco–Wilk–Nusair) the BP (Becke–Perdew) and the B3LYP density functional (DF) methods employed with 6-31G* basis sets. All the methods are shown to reproduce correctly the absorption and resonance Raman spectra in the region corresponding to the low-energy $1^2A_u \rightarrow 1^2B_{3g}$ transition. The discrepancies between the theory and experiment are attributed to a (weak) Dushinsky effect predominately due to a mixing of the $\nu_3 = 1593\text{ cm}^{-1}$ and $\nu_4 = 1342\text{ cm}^{-1}$ vibrations in the 1^2B_{3g} state of the PMDA radical. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The anionic and cationic species are important at least for two reasons. The presence of relatively large cations in the cosmic space is most likely responsible for many infrared bands observed in the emission spectra of the interstellar space [1]. On the other hand, there is an important family of the large aromatic molecules which form the donor–acceptor crystals with acid anhydrides as the electron acceptors [2]. The anthracene–pyromellitic diahydride anion (PMDA) and the pyrene–PMDA crystals offer the well-known examples [2–4]. The better understanding of anions and cations properties in their excited states may be very useful when studying the optical characteristics of the donor–acceptor crystals in terms of the charge-transfer theoretical models [5–7].

The survey of the empirical data for the cations and anions [8–18] teaches us that the absorption and resonance Raman (RR) spectra of radicals show vibrational structures due to activity of the totally symmetric oscillations. The intensity distributions in these spectra are thus governed by the Franck–Condon (FC) effects resulting from the difference in the nuclear equilibrium configurations between the electronic states involved in the absorption and/or emission processes. The analysis of these effects is basically simple when the ground and the excited state(s) geometries can be reached with sufficient accuracy from quantumchemical computations. With the help of the semiempirical [19,20] and/or ab initio methods [20–24], such computations can be readily performed even for large cationic species. On the other hand, the anionic species are much more challenging since the ab initio treatments usually require very extensive basis sets in order to describe properly the electron density in the valance states. Of many methods appropriate to deal with that kind of problems,

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the MCSCF [25] or CASSCF [26,27] methodology is probably most suitable and sophisticated on the formal base. However, certain problems remain, e.g., how large the orbitals active space should be to describe the somewhat subtle changes of the geometry manifested via the FC effects. At this stage, it would be interesting to examine how the less refined, but very practical, quantumchemical methods might be useful to interpret the experimental data available for the relatively large organic anions. The main goal of this Letter is to test the density functional theory (DFT). For this purpose the pyromellitic dihydride (PMDA) anion is taken as an important and illustrative example.

In this Letter we are going to discuss in some detail the FC effects in low-energy excited states of the pyromellitic dihydride (PMDA) anion. The absorption spectrum of that radical measured in the range 14 000–30 000 cm^{-1} evidences two strong dipole-allowed electronic transitions, $1^2A_u \rightarrow 1^2B_{3g}$ and $1^2A_u \rightarrow 1^2B_{1g}$ [18]. Of these two transitions, the lowest energy $1^2A_u \rightarrow 1^2B_{3g}$ one at ca. 15 000 cm^{-1} shows relatively simple vibrational structure due to the activity of the totally symmetric modes. The experiment has shown that only four of the nine totally symmetric vibrations are significantly enhanced in the Raman spectra when exciting the PMDA anion in the region corresponding to the 1^2B_{3g} state [17]. These spectra are subject to our analysis performed in terms of the DFT method applied on different levels of approximation, namely, the local spin density VWN (Vosco–Wilk–Nusair) [28] and the nonlocal spin density BP (Becke–Perdew) [29] approximations. The results of the Becke’s three-parameter hybrid method with the Lee–Yang–Parr correlation functional (B3LYP) [30–32] are also presented. Dealing with the absorption and RR spectra corresponding to the $1^2A_u \rightarrow 1^2B_{3g}$ transition, we neglect the vibronic coupling and we treat the vibrations as the oscillators, which are displaced but not distorted in the excited electronic states. The FC effects in the higher energy 1^2B_{1g} state of the PMDA anion will be discussed in a separate paper.

2. Methods and computational details

The PMDA anion belongs to the D_{2h} point group and possesses the ground electronic state of the A_u

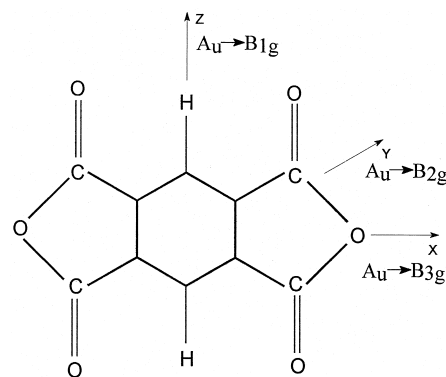


Fig. 1. The geometric structure and the selection rules for the electronic transitions from the ground 1^2A_u state of the PMDA anion.

symmetry. Therefore, only the $A_u \rightarrow B_{3g}$ (x -polarization), $A_u \rightarrow B_{2g}$ (y -polarization) and $A_u \rightarrow B_{1g}$ (z -polarization) electronic transitions are dipole-allowed. The geometrical structure of the PMDA anion and the polarizations of the transition dipole moments are given in Fig. 1.

The equilibrium nuclear configurations in the ground (1^2A_u) and the first dipole-allowed (1^2B_{3g}) states required to determine the FC parameters were found from the geometry optimization procedures available from the GAUSSIAN 94 program package [33]. For purpose of this Letter we employed the B3LYP method [30,31] with 6-31G* basis set. To get a better insight in the quality of the DFT results the computations within the local spin density VWN [28] and the nonlocal spin density BP [29] approximations were also performed with the double numerical functions augmented by polarization functions (DNP). These functions are equivalent to the Pople 6-31G*-type basis set. In all computations the inner core electrons (1s) of the carbon and oxygen atoms were frozen.

Table 1 gives the ground-state frequencies obtained from the B3LYP/6-31G*, VWN/DNP and BP/DNP treatments for the ground (1^2A_u) state of the PMDA anion. For the $1^2A_u \rightarrow 1^2B_{3g}$ transition, the dimensionless FC parameters, $B_{x,i}$ are also listed in Table 1. The FC parameters were directly evaluated from the expression [21]:

$$B_{x,i} = \mathbf{S}_i^T \cdot \mathbf{F}(\mathbf{X}, \mathbf{G}) \left(\frac{\hbar}{\mu_i \omega_i} \right)^{-1}, \quad (1)$$

Table 1

The ground-state frequencies ($\nu_{0,i}$) and the FC parameters ($B_{X,i}$) for the lowest energy dipole allowed 1^2B_{3g} state of the PMDA anion as achieved from B3LYP/6-31G*, VWN/DNP and BP/DNP methods

B3LYP/6-31G*		VWN/DNP		BP/DNP	
$\nu_{0,i}$	($B_{X,i}$)	$\nu_{0,i}$	($B_{X,i}$)	$\nu_{0,i}$	($B_{X,i}$)
3210	(0.05)	3141	(0.03)	3126	(0.03)
1869	(0.03)	1831	(0.04)	1700	(0.05)
1593 [1548] ^a	(0.32)	1590	(0.27)	1494	(0.36)
1342 [1316]	(0.77)	1345	(0.66)	1223	(0.70)
1132 [1110]	(0.31)	1128	(0.35)	1024	(0.43)
755	(0.00)	742	(0.11)	712	(0.02)
641	(0.14)	626	(0.15)	583	(0.20)
484	(0.59)	486	(0.48)	479	(0.41)
279	(0.02)	283	(0.09)	246	(0.20)

^aThe experimental data from Ref. [16].

in which S_i is a column vector containing the Cartesian nuclear displacements in the Q_i normal mode with angular frequency ω_i and reduced mass μ_i ; $F(X, G)$ is the column vector containing the difference of the nuclear position vectors in the excited X ($=1^2B_{3g}$) state and the ground G ($=1^2A_u$) state equilibrium configurations. Applying Eq. (1) to evaluate FC parameters we assumed that the vibrational

(normal) coordinates were the same in the ground and the excited states.

3. Discussion

In the visible and near UV range, 14 000–30 000 cm^{-1} , the absorption spectrum of the PMDA anion shows two intense bands [18]. In this range our DFT computations predict three dipole-allowed transitions: $1^2A_u \rightarrow 1^2B_{3g}$, $1^2A_u \rightarrow 1^2B_{2g}$ and $1^2A_u \rightarrow 1^2B_{1g}$. The $1^2A_u \rightarrow 1^2B_{3g}$ and $1^2A_u \rightarrow 1^2B_{1g}$ transitions are in-plane polarized being $\pi-\pi^*$ in character. Their adiabatic transition energies calculated with the use of the B3LYP/6-31G* method are: $E(1^2B_{3g}) = 14\,309\text{ cm}^{-1}$ and $E(1^2B_{1g}) = 21\,060\text{ cm}^{-1}$. The third extremely weak $1^2A_u \rightarrow 1^2B_{2g}$ transition is polarized along the y-axis of the PMDA and is due to $\pi-\sigma^*$ single electron promotion. The resulting absorption spectrum is therefore quite simple and resembles that one deduced earlier from the Longuet–Higgins and Pople semiempirical method [18].

The left-hand site of Fig. 2 shows the experimental (top curve) and the theoretical absorption spectra

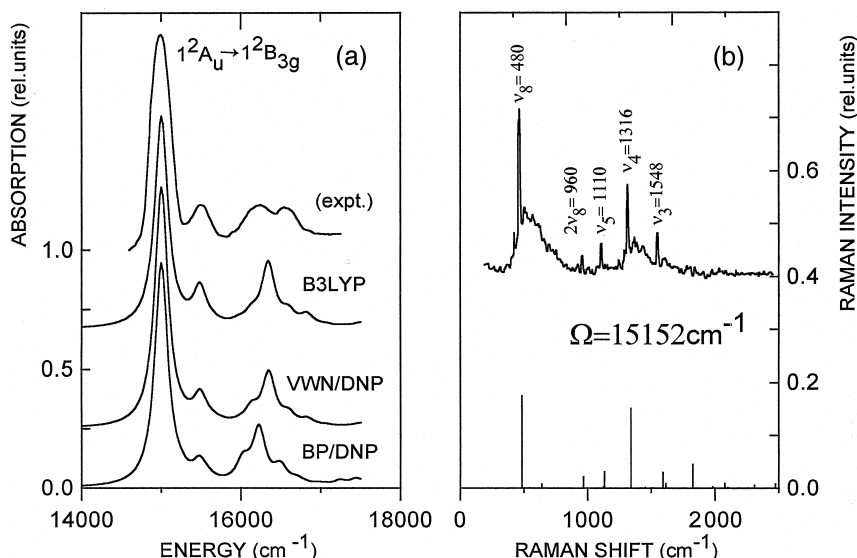


Fig. 2. Comparison between theory and the experiment [17] for the absorption (a) and RR spectra (b) corresponding to the $1^2A_u \rightarrow 1^2B_{3g}$ transition. The linewidth is $\Gamma(1^2B_{3g}) = 100\text{ cm}^{-1}$. The frequencies and the FC parameters are given in Table 1. The RR spectrum was calculated with the B3LYP/6-31G* parameters.

calculated from B3LYP/3-21G*, VWN/DNP and BP/DNP methods in the regions corresponding to the $1^2A_u \rightarrow 1^2B_{3g}$ transition. All of the theoretical spectra were obtained as superpositions of the Lorentzian curves with linewidth $\Gamma(1^2B_{3g}) = 100 \text{ cm}^{-1}$. The right-hand side of Fig. 2 presents the experimental (line) and theoretical (sticks) RR spectra obtained for a laser excitation energy of $\Omega = 15152 \text{ cm}^{-1}$. The theoretical RR spectrum was determined within the vibronic model reported earlier [21]. To facilitate a comparison between the intensities of the different spectra, the calculated origins of the $1^2A_u \rightarrow 1^2B_{3g}$ transition were synchronized to that known from the experiment. So, except for these energy shifts made to improve presentation, no other scaling was made to simulate the absorption and RR spectra depicted in Fig. 2.

Viewing the numbers in Table 1 we can see that the FC parameters in the 1^2B_{3g} state are not large and the three DFT methods predict rather poor FC activity of the totally symmetric vibrations in the region corresponding to the $1^2A_u \rightarrow 1^2B_{3g}$ transition. In fact the absorption spectra in Fig. 2a are dominated by the single-mode transitions, in agreement with the experiment. These transitions can be easily assigned to the vibrations with the ground-state (B3LYP/6-31G*) frequencies: $\nu_8 = 486 \text{ cm}^{-1}$, $\nu_5 = 1132 \text{ cm}^{-1}$, $\nu_4 = 1342 \text{ cm}^{-1}$ and $\nu_3 = 1593 \text{ cm}^{-1}$. A similar conclusion regarding activity of the a_g -symmetry vibrations can be drawn when comparing the theoretical and experimental Raman spectra in Fig. 2b. This spectrum is essentially dominated by the fundamentals of the ν_8 , ν_5 , ν_4 and ν_3 vibrations and only the very weak feature at 960 cm^{-1} can be assigned as the overtone of the ν_8 mode. It is interesting to note that all three VWN/DNP, BP/DNP and B3LYP/6-31G* methods yield very similar intensity patterns which resemble the one observed in the empirical absorption. The same can be proved when comparing the RR spectra obtained from the different DFT methods applied. Nevertheless, it should be noted that the agreement between the theoretical and the experiment absorption is not perfect, especially for the excitation energy near 16500 cm^{-1} . In particular, the three DFT methods and the applied vibronic model overestimate the FC activity of the $\nu_4 = 1342 \text{ cm}^{-1}$ vibration and underestimate the activities of the $\nu_5 = 1132 \text{ cm}^{-1}$ and

$\nu_3 = 1593 \text{ cm}^{-1}$ vibrations in the low-energy $1^2A_u \rightarrow 1^2B_{3g}$ band. Since the absorption spectra in Fig. 2a are so consistent for so different DFT treatments, we surmise that the discrepancies observed near 16500 cm^{-1} may be due to limitations of the vibronic model rather than owing to low-accuracy of the DFT VWN/DNP, BP/DNP and B3LYP/6-31G* methods. Specifically, it is conceivable that the inclusion of the weak mode-mixing (Dushinsky effect) [34,35] in the ν_3 , ν_4 and ν_5 vibrations could improve the agreement between theory and experiment in the debatable region.

In order to illustrate such a possibility, consider the 1^2B_{3g} state vibrational manifold and let the vibrational (dimensionless) normal coordinates Q_i be subject to the mode-mixing effects governed by the second term in the vibrational Hamiltonian:

$$H = \sum_{i=1}^N \frac{\hbar \omega_i}{2} \left[P_i^2 + (Q_i + B_{X,i})^2 \right] + \sum_{i=1}^N \sum_{j \neq 1}^N f_{ij} Q_i Q_j. \quad (2)$$

The coefficients f_{ij} are the Dushinsky's constants. To deal with Hamiltonian (2) we can express the vibrational functions of the 1^2B_{3g} state as

$$\begin{aligned} \Lambda_\lambda(B_{3g}) = & \sum_{\nu_1} \sum_{\nu_2} \cdots \sum_{\nu_N} C_{\nu_1, \nu_2, \dots, \nu_N, \lambda} \xi_{\nu_1} \\ & \times (Q_1 + B_{X,1}) \xi_{\nu_2} (Q_2 + B_{X,2}) \cdots \xi_{\nu_f} \\ & \times (Q_f + B_{X,N}), \end{aligned} \quad (3)$$

where the coefficients $C_{\nu_1, \nu_2, \dots, \nu_N, \lambda}$ can be readily determined from the standard diagonalization procedure if the parameters appearing in the Hamiltonian are known from quantumchemical calculations. Subsequently, the FC overlap integrals, $(\Lambda_0 | \Lambda_\lambda)$ can be straightforwardly found for any $|1^2A_u\rangle \Lambda_0 \rightarrow |1^2B_{3g}\rangle \Lambda_\lambda$ transitions involved in the absorption process.

Fig. 3 shows the absorption spectra calculated for the $1^2A_u \rightarrow 1^2B_{3g}$ transition and for the frequencies and FC parameters obtained within the B3LYP/6-31G* method. For illustrative purposes, two vibrations: $\nu_4 = 1342 \text{ cm}^{-1}$ and $\nu_3 = 1593 \text{ cm}^{-1}$ were allowed for the mode-mixing with $f_{34} = 0$ (solid

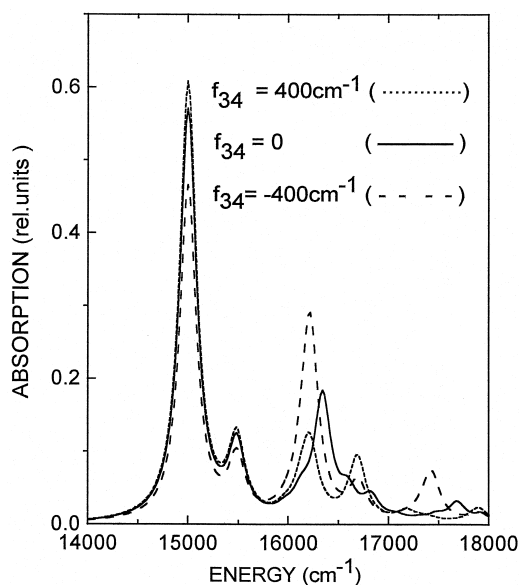


Fig. 3. The absorption spectra calculated with Dushinsky mixing in the $\nu_4 = 1342 \text{ cm}^{-1}$ and $\nu_3 = 1593 \text{ cm}^{-1}$ vibrations; $f_{34} = 0$ (solid line), $f_{34} = 400 \text{ cm}^{-1}$ (dotted line) and $f_{34} = -400 \text{ cm}^{-1}$ (dashed line). The remaining parameters are the same as the B3LYP absorption in Fig. 2a.

line), $f_{34} = -400 \text{ cm}^{-1}$ (dashed line) and $f_{34} = 400 \text{ cm}^{-1}$ (dotted line). It follows from Fig. 3 that even a weak Dushinsky effect causes a splitting of the band at 16500 cm^{-1} and tends to suppress the intensity of the $\nu_4 = 1342 \text{ cm}^{-1}$ mode. Such a behavior is just required to establish the correct intensity distribution in the theoretical absorption of the $1^2A_u \rightarrow 1^2B_{3g}$ band near 16500 cm^{-1} . We have to emphasize that the model sketched above offers a plausible albeit very simple explanation of the observed discrepancies between the theory and experiment. For a full verification of the model prediction, it is necessary to know the complete set of the mode-mixing parameters, f_{ij} . These should be, at least in principle, obtainable from the quantumchemical computations. While the determination of the Dushinsky's parameters from quantumchemical computations is basically straightforward, it would lead us beyond the main goal of this Letter. So, in the interest of brevity we postpone the discussion of that problem to a subsequent paper [36]. For the same reason the results of DFT computations regarding the FC effects in the 1^2B_{1g} will be reported in the separate paper.

4. Conclusion

In this Letter we have discussed the FC effects in the lowest energy dipole-allowed 1^2B_{3g} state of the PMDA anion radical. In the discussion we have applied three approaches of DFT theory, namely, VWN/DNP, BP/DNP and B3LYP/6-31G*. They were used to evaluate the FC parameters and then applied to reconstruct the absorption and the RR spectra corresponding to the $1^2A_u \rightarrow 1^2B_{3g}$ transition. Although all three DFT methods are essentially different on the formal base, they reproduce quite correctly the main features of the experimental absorption. A similar conclusion can be drawn when the calculated and the measured RR spectra at $\Omega = 15152 \text{ cm}^{-1}$ are compared. Some differences between the calculated and measured absorption were noticed in the region near 16500 cm^{-1} . We have shown that these differences could be eliminated if the vibronic model is extended in order to include the mode-mixing (Dushinsky) effects. The estimates indicate that the strongest effects arise due to the rotation of two normal modes with the frequencies $\nu_4 = 1342 \text{ cm}^{-1}$ and $\nu_3 = 1593 \text{ cm}^{-1}$. Nevertheless, a weak mixing of these modes with other ones is also likely in the 1^2B_{3g} state of the PMDA anion radical [36].

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References

- [1] L.J. Allamandola, in: S. Cyvin, J. Gutman (Eds.), Topic in Current Chemistry, Springer, Berlin, 1990.
- [2] D. Haarer, M.R. Philpott, in: V.M. Agranovich, R.M. Hochstrasser (Eds.), Spectroscopy and Excitation Dynamics of Condensed Molecular Systems, Chap. 2, North-Holland, 1983, p. 27.

- [3] T. Asahi, Y. Matsuo, H. Masuhara, *Chem. Phys. Lett.* 256 (1996) 525.
- [4] M. Assel, T. Höfer, A. Laubereau, W. Keiser, *J. Phys. Chem.* 100 (1996) 11836.
- [5] D.P. Craig, P. Petelenz, *Chem. Phys. Lett.* 105 (1984) 17.
- [6] I.V. Brovchenko, A. Eilmes, P. Petelenz, *J. Chem. Phys.* 98 (1993) 3737.
- [7] P. Petelenz, M. Slawik, K. Yokoi, M.Z. Zgierski, *J. Chem. Phys.* 105 (1996) 4427, and the references cited therein.
- [8] P.C. Li, J.P. Devlin, H.A. Pohl, *J. Phys. Chem.* 76 (1972) 1026.
- [9] C. Takahashi, S. Maeda, *Chem. Phys. Lett.* 22 (1973) 364.
- [10] R. Bazio, A. Girlando, C. Pacile, *J. Chem. Soc., Faraday Trans.* 71 (1975) 1237.
- [11] A. Girlando, R. Bazio, C. Pacile, *Chem. Phys. Lett.* 25 (1974) 403.
- [12] C.K. Chi, E.R. Nixon, *Spectrochim. Acta, Part A* 31 (1975) 1739.
- [13] D.L. Jeanmaire, R.P. Van Duyne, *J. Am. Chem. Soc.* 98 (1976) 4029.
- [14] D.L. Jeanmaire, R.P. Van Duyne, *J. Am. Chem. Soc.* 98 (1976) 4034.
- [15] C. Takahashi, S. Maeda, *Chem. Phys. Lett.* 24 (1974) 584.
- [16] T. Shida, S. Iwata, *J. Am. Chem. Soc.* 95 (1973) 3473.
- [17] S.J. Sheng, G. Hug, *Chem. Phys. Lett.* 57 (1978) 168.
- [18] T. Shida, S. Iwata, M. Imamura, *J. Phys. Chem.* 78 (1974) 741.
- [19] G. Orlandi, F. Zerbetto, M.Z. Zgierski, *Chem. Rev.* 91 (1991) 867.
- [20] F. Negri, M.Z. Zgierski, *J. Chem. Phys.* 100 (1994) 1387.
- [21] T. Andruniow, K. Zborowski, M. Pawlikowski, *Chem. Phys. Lett.* 259 (1996) 193.
- [22] T. Andruniow, M. Pawlikowski, *Chem. Phys.* 236 (1998) 25.
- [23] T. Andruniow, M. Pawlikowski, *Chem. Phys.* 236 (1998) 35.
- [24] T. Andruniow, M. Pawlikowski, *Acta Phys. Pol.* 93 (1998) 707.
- [25] K. Ruedenberg, M.W. Smidt, M.M. Gilbert, S.T. Elbert, *Chem. Phys.* 71 (1982) 41, and references therein.
- [26] K. Andersson, P.A. Malmqvist, B.O. Roos, A.J. Sadlej, K. Wolinski, *J. Phys. Chem.* 94 (1990) 5483.
- [27] K. Andersson, B.O. Roos, in: R. Yarkony (Ed.), *Modern Electron Structure Theory, Multiconfigurational Second-order Perturbational Theory*, vol. 1, World Science, Singapore, 1994, and references therein.
- [28] S.H. Vosco, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1990) 1200.
- [29] J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822.
- [30] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [31] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [32] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P. von R. Schleyer, *J. Comp. Chem.* 4 (1983) 291, and references cited therein.
- [33] M.J. Frisch et al., *GAUSSIAN 94 Revision E.1*, Gaussian, Pittsburgh, 1995.
- [34] W. Siebrand, M.Z. Zgierski, in: E.C. Lim (Ed.), *Excited States*, vol. 4, Chap. 1, Academic Press, New York, 1979.
- [35] H. Kupka, P.H. Cribb, *J. Chem. Phys.* 85 (1986) 1303.
- [36] T. Andruniow, M. Pawlikowski, M.Z. Zgierski, *J. Phys. Chem. A* 104 (2000) 845.