



Forbidden transitions in benzene

I. Borges Jr.^{a,*}, A.J.C. Varandas^a, A.B. Rocha^b, C.E. Bielschowsky^c

^aDepartamento de Química, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal

^bInstituto de Física, Universidade Federal do Rio de Janeiro Cidade Universitária, CT Bloco A, Caixa Postal 68528, Rio de Janeiro 21945-970, RJ, Brazil

^cDepartamento de Físico-Química, Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária CT Bloco A, Rio de Janeiro 21949-900, RJ, Brazil

Accepted 18 July 2002

Abstract

We have computed the optical oscillator strengths for the symmetry-forbidden transitions $1^1B_{2u} \leftarrow \tilde{X}$ and $1^1B_{1u} \leftarrow \tilde{X}$ of benzene through vibronic coupling. Electronic transition dipole moments were calculated at the complete active space self consistent field level along the normal coordinates. Optical oscillator strengths for the sum of the total vibronic excitations are compared with available theoretical and experimental results.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Herzberg–Teller effect; Vibronic coupling; Complete active space self consistent field wavefunctions

1. Introduction

The optical spectra of benzene in the transition energy range from 4.5 to 7 eV show several vibronic bands related to three electronic excitations from the ground state, namely, to the 1^1B_{2u} , 1^1B_{1u} and 1^1E_{1u} , with the maximum peak intensities at 4.9, 6.19 and 6.96 eV, respectively [1]. The lowest valence transitions $1^1B_{2u} \leftarrow \tilde{X}$ and $1^1B_{1u} \leftarrow \tilde{X}$ are strictly forbidden on symmetry grounds and under a Franck–Condon (i.e. vertical) approach. However, through vibrations of the benzene framework (i.e. vibronic coupling), such transitions become optically

accessible. The sum of the optical oscillator strengths (OOS) for each of the vibronic bands 1^1B_{2u} , 1^1B_{1u} and 1^1E_{1u} excited states are in the ratio 1:10:100 [1].

The theory of vibronic coupling and intensity of symmetry-forbidden transitions [2] have been established long ago by Herzberg and Teller [3]. They have set the principles that control which normal vibrations make a transition allowed, and how to calculate band intensities from the knowledge of the molecular electronic wave functions in its equilibrium nuclear configuration. Murrell and Pople [4] applied the Herzberg–Teller theory to the 1^1B_{2u} and 1^1B_{1u} transitions in benzene to obtain relative intensities. Albrecht [5], and Roche and Jaffé [6], have also studied these transitions. All such works have in common the use of perturbation theory. Ziegler and Albrecht [7] employed CNDO/S semiempirical electronic wave functions to calculate transition dipole moments along normal coordinates assuming that the matrix elements

* Corresponding author Present address: Departamento de Físico-Química, Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CT Bloco A, Rio de Janeiro 21949-900, RJ, Brazil.

E-mail address: qtitamar@ci.uc.pt (I. Borges).

vary linearly as a function of the displacement. Metz et al. [8] studied the B_{2u} transition using also CNDO wave functions but taking into account a possible coupling of the electronic excited states by more than one vibration. This may lead to a rotation of the normal coordinates with respect to each other, known as the Duchinsky effect [9]. Orlandi et al. [10] employed a similar framework for the B_{2u} transition, namely, perturbation theory and inclusion of the Duchinsky effect, but used configuration interaction with single (CIS) electronic excitation wave functions and empirical force fields. All these works presented optical oscillator strengths summed over the vibrational bands.

Recently, simulation of the vibronic spectra of the B_{2u} [11,12] and also of the B_{1u} transitions [13] in benzene have been published. These works employed electronic wave functions at the Complete active space self consistent field (CASSCF) level with six active π orbitals. Berger et al. [11] and Schumm et al. [12] applied a Franck–Condon approach and used techniques to solve the involved multidimensional integrals, but reported only relative vibrational band intensities. Bernhardsson et al. [13] computed the harmonic force fields for the ground and excited states at the CASSCF level employing analytical derivatives of the transition dipole moment and energy. However, they assumed a linear approximation for the dependence of the transition dipole as function of the nuclear displacement coordinates. Using multiconfigurational second-order perturbation theory (CASPT2) to calculate the transition energies, they reported absolute oscillator strengths for the main vibronic bands.

In this work, we report calculations of the OOS for the symmetry-forbidden transitions $1^1B_{2u} \leftarrow \tilde{X}$ and $1^1B_{1u} \leftarrow \tilde{X}$ of benzene through vibronic coupling. These transitions, studied theoretically with a variety of approaches, can provide a good testing ground for the methodologies involved. We have employed the closure relation to sum all contributions from the vibronic levels of the excited state and computed explicitly the electronic transition dipole moments along the relevant normal coordinates for the ground electronic state vibrational modes using the CASSCF method. The computational approach resembles closely the one followed by Ziegler and Albrecht [7] but does not rely on a linear approximation for the dependence of the transition dipole moment as function of the displacements. The methodology was success-

fully applied by two of us to forbidden transitions in H_2CO and CO_2 [14], CH_4 [15], and acetone [16], being summarized in Section 2. Section 3 presents our results and comparisons with theoretical and experimental data. The conclusions are in Section 4.

2. Theoretical framework

The starting point of the calculation is the Born–Oppenheimer approximation for the total wave function,

$$\Psi_{kv} = \psi_k(\mathbf{r}; \mathbf{Q})\chi_{kv}(\mathbf{Q}) \quad (1)$$

where \mathbf{r} represents the coordinates of the electrons and \mathbf{Q} the coordinates of the nuclear vibrational normal modes. In turn, ψ_k and χ_{kv} are the electronic and vibrational wave functions for the (k, v) vibronic state.

The optical oscillator strength $f(E)_{kv \leftarrow 00}$ for excitation from the $v = 0$ vibrational level of the ground electronic state $k = 0$ to the v vibrational level of the k th electronic state assumes the form

$$f(E)_{kv \leftarrow 00} = \frac{2}{3} \Delta E g_k |\langle \chi_{kv}(\mathbf{Q}) | M_{0k}(\mathbf{Q}) | \chi_{00}(\mathbf{Q}) \rangle|^2 \quad (2)$$

where ΔE is the excitation energy of the vibronic transition $kv \leftarrow 00$, and the electronic transition dipole moment is given by

$$M_{0k}(\mathbf{Q}) = \left\langle \psi_k(\mathbf{r}; \mathbf{Q}) \left| \sum_{i=1}^n r_i \right| \psi_0(\mathbf{r}; \mathbf{Q}) \right\rangle \quad (3)$$

with g_k being the degeneracy of the final state (1 or 2).

Summing over all discrete vibrational levels (and integrating over the continuum) of the k th electronic band, replacing the transition energy ΔE by an average value \bar{E} and using the closure relation of the upper (k) state, we obtain for the total intensity of the whole band [4] the following result:

$$\begin{aligned} f(E)_{k \leftarrow 0} &= \sum_v f(E)_{kv \leftarrow 00} \\ &= \frac{2}{3} \sum_v \Delta E g_k |\langle \chi_{kv}(\mathbf{Q}) | M_{0k}(\mathbf{Q}) | \chi_{00}(\mathbf{Q}) \rangle|^2 \\ &= \frac{2}{3} \bar{E} g_k \langle \chi_{00}(\mathbf{Q}) | M_{0k}^2(\mathbf{Q}) | \chi_{00}(\mathbf{Q}) \rangle \end{aligned} \quad (4)$$

Note that in this expression only the normal modes of the ground state are involved and transitions are from the ground vibrational state ($v = 0$).

We now assume that the total dipole transition moment is the sum of the transition dipole moments for each normal mode vibration L that contributes to the band intensity. One then gets,

$$M_{0k}(\mathbf{Q}) = \sum_L M_{0k}(Q_L) \\ = \sum_L \left\langle \psi_k(\mathbf{r}; Q_L) \left| \sum_{i=1}^n r_i \right| \psi_0(\mathbf{r}; Q_L) \right\rangle \quad (5)$$

In turn, the nuclear wave function χ_{00} is expressed in the framework of this harmonic approximation as

$$\chi_{00}(Q_1, Q_2, \dots, Q_J) = \prod_{L=1}^J \xi_L(Q_L), \quad (6)$$

where $\xi_L(Q_L)$ are the wave functions of each normal mode in the ground state. Combining Eqs. (4)–(6), we obtain for the OOS summed over the vibrational modes of the k th excited state

$$f(\bar{E}) = \frac{2}{3} \bar{E} g_k \sum_L \langle \xi_L(Q_L) | M_{0k}^2(Q_L) | \xi_L(Q_L) \rangle \quad (7)$$

The integral in Eq. (7) over the harmonic functions $\chi_{00}(Q_L)$ is straightforward. We have done calculations of $M_{0k}(Q_L)$ at the CASSCF level for several values of Q_L in each normal mode that contributes to the vibronic coupling. We have then expanded $M_{0k}^2(Q_L)$ as a power series,

$$M_{0k}^2(Q_L) = M_{0k}^2(0) + a_1(Q_L) + a_2(Q_L)^2 + \dots \quad (8)$$

where $\{a_j\}$ are numerical constants obtained through fitting of the calculated CASSCF values. If the transition is optically forbidden, the first term in Eq. (8) should be zero, otherwise it will be expected to be the dominant one. For a dipole forbidden transition, the other expansion terms account for the transition intensity. We emphasize that Eq. (8) does not employ the Franck–Condon approximation.

3. Results and discussion

3.1. Electronic structure calculations

The CASSCF space was built from six valence π orbitals and six electrons, usually denoted as CAS(6,6). Such a space has been shown by Roos

et al. [17] to be adequate to describe the energy surfaces of the two lowest electronic states (B_{2u} and B_{1u}) and corresponding $\pi \rightarrow \pi^*$ transitions, at least close to the equilibrium geometries [13]. The molecular orbitals to calculate the transition dipole moments were state averaged for each transition, an approach that improves the accuracy of the transition dipole moments by providing a balanced description of each pair of states [17]. We have employed the correlation consistent double-zeta (cc-pvdz) basis set of Dunning [18] for the computation of the transition dipole moments while for the ground state frequencies and optimization we have used the 6-31G** basis set of Pople and coworkers [19]. For each normal mode, the ground state CASSCF frequencies employed to compute the harmonic integrals in Eq. (7) have been scaled by 0.92. This value has been chosen to match the calculated ground CH stretch frequency (mode ν_7) to the experimental one [20], an approach similar to that followed by Liao et al. [21] in their work on acetone. Our computed vertical transition energies for each state are 4.90 eV (B_{2u}) and 6.20 eV (B_{1u}), which can be compared with the CASPT2 values of Bernhardsson et al. [13], 4.52 and 5.98 eV, and with the coupled-cluster with singles and doubles substitutions (CCSD) calculation [22] for the B_{2u} state of 5.07 eV. This favorable comparison between our CASSCF vertical energies and other results, which employed large basis sets, is possibly due to a compensation of errors resulting from the neglect of dynamical correlation and our use of a double- ζ basis set. We have then used our calculated CASSCF vertical energies as the average energy \bar{E} in Eq. (4) to obtain the oscillator strengths for each normal mode. All ab initio calculations have been carried out using the MOLPRO suite of programs [23].

3.2. The $1^1B_{2u} \leftarrow \tilde{X}$ transition

The dipole moments belong to the e_{1u} (x and y in-plane components) and a_{2u} (z out-of-plane component) irreducible representations (D_{6h} symmetry). Thus, this transition is optically forbidden by symmetry reasons, and hence the first term in the expansion of Eq. (8) should vanish [24]. However, through the vibrations of e_g and b_{1g} symmetries, higher-order terms will become nonzero. Since there is no b_{1g} vibration in benzene, only the in-plane e_{2g}

Table 1
Fitted expansion coefficients in Eq. (8) for each vibrational mode in the transition $1^1B_{2u} \leftarrow \tilde{X}$

Mode	a_1	a_2	a_3
ν_6	-0.000390958	0.0521071	0.0
	0.00175363	0.408109	0.0
ν_7	-0.000264503	0.0203879	0.0
	-0.00312601	0.0346724	0.0
ν_8	-5.1986(-6)	0.00390324	-0.00210251
	1.40268(-5)	0.00398927	-0.00141568
ν_9	3.20194(-5)	0.00749876	0.00231767
	-3.05214(-5)	0.00800146	0.0

In parentheses are the powers of ten by which each number should be multiplied.

degenerate modes ν_6 , ν_7 , ν_8 , and ν_9 will contribute in first-order to the band intensity [13].

Table 1 shows, for each active mode, the expansion coefficients in the least-squares fits of the computed $M_{0k}^2(Q_L)$ values using Eq. (8). Some of the fits included only up to second-order terms, and some to third-order. Note that, for the expansion of the transition dipole squared in Eq. (8), it is necessary to consider only positive values of the displacement along a normal coordinate since $M_{0k}^2(Q_L)$ is an even function [16] for the normal modes considered here. Table 1 shows also the different contributions of each component of the e_g degenerate modes which could be independently calculated in our approach.

In Table 2 we present the total integrated OOS and the contribution from each vibrational normal mode to the 1^1B_{2u} transition, and other available results. Although Metz et al. [8] claim that the inclusion of

the Duchinsky effect may raise the theoretical results for this transition by some 20%, the experimental results of Fischer et al. [25] have not shown any marked contribution of the Duchinsky effect. We have not included this effect in our calculations.

The experimental spectra around the 4.9 eV region show more than 25 vibronic bands originated from the ν_6 , ν_7 , ν_8 and ν_9 inducing modes. The vibronic bands from the ν_6 inducing mode is responsible for about 90% of the total OOS, and their components $6_0^1 1_0^n$ ($n = 0-5$) are clearly identified in the optical spectra. The other vibronic modes, from the ν_7 , ν_8 and ν_9 inducing modes, are not as easily identified in the optical spectra as the mode ν_6 and, as expected, Table 2 shows some discrepancy concerning the relative intensities of the experimental results. In particular, the experimental results of Callomon [26] do not report any contribution from the ν_8 mode, and the measurement of Stephenson et al. [27] shows a contribution of 0.6%.

The sum of $6_0^1 1_0^n$ ($n = 0-5$) absolute OOS results of the jet-cooled experimental results of Hiraya and Shobatake [28] differs from the vapor (room temperature) measurements of Pantos et al. [1]. This discrepancy might be a combination of experimental normalization problems due to the low intensity of these bands (about 1/100 of those originated from the E_{1u} excited state) and contribution of hot bands in the room temperature measurements of Pantos et al. [1]. The latter was pointed out by Hiraya and Shobatake [28].

Table 2 shows that, except for the results of Ziegler and Albrecht [5] and Metz et al. [8], the other

Table 2
Integrated optical oscillator strengths divided by 10^{-4} ($f/10^{-4}$) for the transition $1^1B_{2u} \leftarrow \tilde{X}$

Mode	Theoretical ^a					Experimental			
	This work	Ref. [8]	Ref. [10]	Ref. [13]	Ref. [7]	Ref. [27]	Ref. [26]	Ref. [1]	Ref. [28]
ν_6	3.348 (100.0)	5.9 (100.0)	(100.0)	(100.0)	4.98 (100.0)	(100.0)	(100.0)	4.7 ± 0.94	6.48
ν_7	0.1222 (3.7)		(3.0)	(5.8)	0.08 (1.7)	(3.6)	(5.9)		
ν_8	0.1341 (4.0)	1.38 (23)	(5.8)	(0.4)	2.48 (49.8)	(0.6)	-		
ν_9	0.1965 (3.6)		(0.3)	(4.0)	0.4 (8.3)	(1.8)	(2.3)		
Total	3.80	7.28		5.35	7.94				

The contributions from each inducing mode are also given. Normalized values are indicated in brackets.

^a Other theoretical results: Roche and Jaffé [6] reported 9.0×10^{-4} while Albrecht [5] calculated 60.0×10^{-4} .

theoretical and experimental results agree that the inducing ν_6 mode is responsible for about 90% of the total OOS of these vibronic bands. Nevertheless, they do agree, in general, for the absolute values of for the OOS as well as on the relative contributions of the other inducing modes (ν_7 , ν_8 and ν_9).

The theoretical results presented in Table 2 employed different methods both in the calculations of the wave functions, used to determine the electronic matrix elements, and in the method utilized to determine the vibronic coupling. Table 2 shows that they can affect both the absolute values, and the relative contributions of the different inducing modes.

Among the methods that considered perturbation theory to calculate the vibronic coupling, the early results of Albrecht [5] clearly overestimates the intensities of these vibronic bands. Both Roche and Jaffé [6] and Metz et al. [8] used the semiempirical CNDO function, although the latter took into account a possible coupling of the electronic states by more than one vibration. Their total OOS values differ by some 20% and are larger than the experimental results. Unfortunately, Orlandi et al. [10] presented only relative values for the OOS. Their results seems to underestimate the ν_9 inducing mode intensity and overestimate the intensity of the ν_8 inducing mode, a trend also observed in the Metz et al. [8] calculations.

Ziegler and Albrecht [7] directly calculated the OOS employing a procedure similar to the present work, and used CNDO semiempirical wave functions. Their total OOS value presented a good agreement with the other CNDO results, and also overestimate both ν_8 and ν_9 inducing modes.

The theoretical results of Bernhardsson et al. [13] employed a CASSCF wavefunction, similar to the one used in the present calculations. Both sets of the total OOS values are lower than the other theoretical values, the results of Bernhardsson et al. [13] being within the reported error bars for both sets of experimental results [1,28] while the present results are within only one of the experimental results of Pantos et al. [1]. While both sets of calculations roughly agrees in the contributions of the ν_7 and ν_9 inducing modes, the present calculations indicate a larger contribution from the ν_8 than the calculations of Bernhardsson et al. [13] and the measurements of Callomon [26] and Stephenson et al. [27].

One should bear in mind when comparing all these results that, except for the contributions of the $6_0^1 1_0^n$ ($n = 0-5$) for the ν_6 inducing mode, the other experimental contributions from the $1^1 B_{2u}$ are difficult to determine. The reason is that they correspond to very low intensity vibronic bands (about 1/100 of those bands from the $1^1 E_{1u}$ excited state) and the ν_7 , ν_8 and ν_9 inducing modes are related to more than 20 vibronic bands not easily attributed in the experimental spectrum. Therefore, we suggest new experimental measurements in order to further investigate these bands and clarify the comparisons with the theoretical results.

3.3. The $1^1 B_{1u} \leftarrow \tilde{X}$ transition

The theoretical study of this transition is more complicated than the previous one: the B_{1u} state is the second valence one, its surface is flat and distorted [13], and other modes contribute to the band intensity. The direct products of the irreducible representations $b_{1u} \otimes e_{1u} \otimes a_{1g} = e_{2g}$ and $b_{1u} \otimes a_{2u} \otimes a_{1g} = b_{2g}$ show that in addition to the e_{2g} normal mode one should include for this transition also the b_{2g} modes.

The total OOS value for the $1^1 B_{1u}$ is experimentally easier to determine than for the $1^1 B_{2u}$, because it is about 10 times more intense. In fact, the experimental results of Pantos et al. [1] and Brith et al. [29] are in good agreement. Unfortunately, the same is not true with respect to the relative contribution of the different inducing modes. The spectrum in this region presents an ambiguous vibronic attribution [28]. Therefore, the measured contributions of the inducing modes should be considered only as indicative.

Table 3 shows the expansion coefficients for the $M_{0k}^2(Q_L)$ values fitted to Eq. (8), while Table 4 reports the computed OOS integrated results.

Except for the theoretical results of Roche and Jaffé [6], all the other calculations presented OOS values in fair agreement with the experimental results. The calculations of Roche and Jaffé [6], that employed perturbation theory to account for the vibronic coupling and CNDO semiempirical wave functions, strongly disagree with other experimental and theoretical results.

Table 3
Fitted expansion coefficients a_j (Eq. (8)) for each vibrational mode in the transition $1^1B_{1u} \leftarrow \tilde{X}$

Mode	a_1	a_2	a_3
ν_4 (b_{2g})	0.00684408	0.222355	0.0
ν_5 (b_{2g})	0.00049087	0.301856	0.0
ν_6 (e_{2g})	0.00176049	0.147245	0.0
	−0.0577821	0.455573	0.0
ν_7 (e_{2g})	−0.154862	0.393867	0.0
	0.025835	0.340117	0.0
ν_8 (e_{2g})	−0.0179871	5.58911	−4.92994
	−0.0330724	5.74406	−4.99192
ν_9 (e_{2g})	0.151295	20.3112	−43.3372
	−0.00714074	25.7285	−43.3372

Note that the e_g modes are degenerate.

Table 3 shows that the present results and the theoretical results of Ziegler and Albrecht [7] do not agree on the relative contributions of the inducing modes. Despite the fact that Ziegler and Albrecht [7] employed the CNDO semiempirical wave function and the present work considered the ab initio CASSCF method, both sets of calculations predicted similar total OOS values for these transition.

When we compare the present results and those of Bernhardsson et al. [13] in Table 3 which also employed ab initio CASSCF wave functions, we see that both calculations agree that the major contribution comes from the ν_9 induced mode followed by the ν_8 mode. On the other hand, we estimate a lower contribution to the vibronic bands coming from the ν_6 than did Bernhardsson et al. [13]. Concerning this

transition, contrary to the previous transition, the present results for the total OOS show a better agreement with the experimental results [1,29] than those of Bernhardsson et al. [13].

It is interesting to observe that the older theoretical result of Ziegler and Albrecht [7] and Roche and Jaffé [6], both with CNDO wave functions, as well as the experimental measurements, assign the largest contribution to the ν_8 normal mode, followed by the ν_6 mode. The present results and the other CASSCF [13] calculations clearly indicate that the main contribution come from the ν_9 inducing mode followed by ν_8 . Since the experimental spectrum in this region does not present an immediate interpretation [28], we strongly suggest a new experimental analysis.

4. Conclusions

We have reported calculations of OOS for the forbidden transitions $1^1B_{2u} \leftarrow \tilde{X}$ and $1^1B_{1u} \leftarrow \tilde{X}$ of benzene through vibronic coupling. Employing a methodology successfully used before for several molecules [14–16], we could present the contributions to the OOS from each normal mode in each transition. Results have compared favorably with recent theoretical calculations for both transitions [13], including the contributions from each mode. Good general agreement is also observed for the total OOS. These transitions in the benzene molecule being studied very much, the approach followed in the present work suggests itself as a viable one.

Table 4
Integrated OOS divided by 10^{-4} ($f/10^{-4}$) for the transition $1^1B_{1u} \leftarrow \tilde{X}$

Mode	This work	Ref. [13]	Ref. [7]	Ref. [6]	Ref. [29] (exp.)	Ref. [1] (exp.)
ν_4 (b_{2g})	9.863 (1.3)	–	0.6	10	0	
ν_5 (b_{2g})	8.137 (1.1)	(2.6)	–	–	0	
ν_6 (e_{2g})	14.33 (1.9)	(8.1)	162.8	150	190	
ν_7 (e_{2g})	9.838 (1.3)	–	6.6	0.0	0	
ν_8 (e_{2g})	239.9 (31.8)	(30.0)	681.6	2000	750	
ν_9 (e_{2g})	754.0 (100.0)	(100.0)	58.8	100	0	
Total	1036	760	910	2300	940 ± 94	900 ± 180.0

The contributions from each inducing mode are also given. In brackets are the normalized quantities. Except for Ref. [29], the other results are from theoretical calculations.

Acknowledgements

IBJr and AJCV gratefully acknowledge the support of Fundação para a Ciência e Tecnologia, Portugal, under programme PRAXIS XXI. ABR and CEB thank CNPq, FAPERJ, and F. José Bonifácio Brazilian agencies, for partial financial support.

References

- [1] E. Pantos, J. Philis, A. Bolovinos, *J. Mol. Spectrosc.* 72 (1978) 36.
- [2] H. Köppel, W. Domcke, L. Cederbaum, Multimode molecular dynamics beyond the Born–Oppenheimer approximation, *Adv. Chem. Phys.* 57 (1984) 59.
- [3] G. Herzberg, E. Teller, *Z. Phys. Chem. B* 21 (1933) 410.
- [4] J.N. Murrell, J.A. Pople, *Proc. Phys. Soc. Lond. A* 69 (1956) 245.
- [5] A.C. Albrecht, *J. Chem. Phys.* 33 (1960) 169.
- [6] M. Roche, H.H. Jaffé, *J. Chem. Phys.* 60 (1974) 1193.
- [7] L. Ziegler, A.C. Albrecht, *J. Chem. Phys.* 60 (1974) 3558.
- [8] F. Metz, M.J. Robey, E.W. Schlag, F. Dörr, *Chem. Phys. Lett.* 51 (1977) 8.
- [9] G.J. Small, *J. Chem. Phys.* 54 (1971) 3300.
- [10] G. Orlandi, P. Palmieri, R. Tarroni, F. Zerbetto, M.Z. Zgierski, *J. Chem. Phys.* 100 (1994) 2458.
- [11] R. Berger, C. Fischer, M. Klessinger, *J. Phys. Chem. A* 102 (1998) 7157.
- [12] S. Schumm, M. Gerhards, K. Kleinermanns, *J. Phys. Chem. A* 104 (2000) 10648.
- [13] A. Bernhardsson, N. Forsberg, P.-A. Malmqvist, B.O. Roos, *J. Chem. Phys.* 112 (2000) 2798.
- [14] A.B. Rocha, C.E. Bielschowsky, *Chem. Phys.* 253 (2000) 51.
- [15] A.B. Rocha, C.E. Bielschowsky, *J. Mol. Struct. (Theochem)* 539 (2001) 145.
- [16] A.B. Rocha, C.E. Bielschowsky, *Chem. Phys. Lett.* 337 (2001) 331.
- [17] B.O. Roos, K. Andersson, M.P. Fülscher, *Chem. Phys. Lett.* 192 (1992) 5.
- [18] T.H. Dunning, *J. Chem. Phys.* 90 (1989) 1007.
- [19] W.J. Hehre, R. Ditchfield, J.A. Pople, *J. Chem. Phys.* 62 (1972) 2921.
- [20] L. Goodman, A.G. Ozkabak, S.N. Thakur, *J. Phys. Chem.* 95 (1991) 9044.
- [21] D.W. Liao, A.M. Mebel, M. Hayashi, Y.J. Shiu, Y.T. Chen, S.H. Lin, *J. Chem. Phys.* 111 (1999) 205.
- [22] O. Christiansen, J.F. Stanton, J. Gauss, *J. Chem. Phys.* 108 (1998) 3987.
- [23] H.-J. Werner, P.J. Knowles, with contributions of R.D. Amos, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Leininger, R. Lindh, A.W. Lloyd, W. Meyer, M.E. Mura, A. Nicklab, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, A.J. Stone, T. Thorsteinsson, *MOLPRO*, 2000.
- [24] D.C. Harris, M.D. Bertolucci, *Symmetry and Spectroscopy: an Introduction to Vibrational and Electronic Spectroscopy*, Dover, New York, 1989.
- [25] G. Fisher, S. Jakobson, R. Naaman, *Chem. Phys. Lett.* 49 (1977) 427.
- [26] J.H. Callomon, T.M. Dunn, I.M. Mills, *Philos. Trans. R. Soc. Lond., Ser. A* 259 (1966) 499.
- [27] T.A. Stephenson, P.L. Radloff, S.A. Rice, *J. Chem. Phys.* 81 (1984) 1060.
- [28] A. Hiraya, K. Shobatake, *J. Chem. Phys.* 94 (1991) 7700.
- [29] M. Brith, R. Lubart, I.T. Steinberger, *J. Chem. Phys.* 54 (1971) 5104.