FLUORESCENCE FROM VIBRONIC STATES OF 1-12 - BENZPERYLENE, IN CONDENSED PHASE

MARIA ESTELA PEREIRA
Departamento e Centro de Física (INIC)
Universidade de Aveiro, 3800 Aveiro, Portugal

(Received 22 June 1983)

ABSTRACT — 1-12 – benzperylene shows fluorescence occurring at energies above the $S_1 \rightarrow S_0$ transition, that is shown to come from four mainly thermally populated vibronic states, being identified the antisymmetrical modes active in the mixing between S_1 and S_2. The rate of vibrational redistribution of the vibronic states energies is shown to be much smaller than the usual rates of pure vibrational states. The intensity of the vibronic bands can be accounted for considering the breakdown of Born – Oppenheimer approximation, using some simplifying assumptions.

1 — INTRODUCTION

Apart from azulene, that shows fluorescence from the second excited state (S_2) due to a rather unusual large energy gap between the first excited state (S_1) and S_2, and has been studied in detail [1], most aromatic hydrocarbon molecules show fluorescence originating only in S_1, irrespective of the state reached in excitation. This fact, known as Kasha's rule [2], is due to a very fast internal conversion between excited states, and is verified both in solution and in the gas phase, even when, in the latter instance, the molecules can be considered as isolated during the lifetime of the excited state.

Using more sensitive spectrometers, it has been possible to see that several other molecules show "anomalous" fluorescence from states with energy above S_1, as pyrene and 3-4 - benzpyrene [3]. This class of molecules has in common a rather small energy gap between S_1 and S_2 (typically 1000-3000 cm^{-1}) and also the fact that while the transition from the ground state (S_0) to S_2 is strongly allowed, the transition $S_0 \rightarrow S_1$ is weak, being usually symmetry forbidden. A review of molecules in this class can be found in the literature [4].

Whilst in these molecules absorption to S_2, being allowed, can be considered as a pure electronic transition, with a vibrational progression due to the different equilibrium coordinate of a symmetrical vibrational mode (in aromatic hydrocarbons usually the C - C stretching mode at 1400 cm^{-1}) absorption to S_1 is dominated by vibronic peaks, occurring at energies above the $S_0 \rightarrow S_1$ energy gap equal to the energy of an antisymmetrical vibrational mode ($\hbar \omega_a$). These peaks have been explained by Herzberg and Teller [5] as a departure from the Condon approximation, due to a mixing of S_1 and S_2 with the assistance of that mode. Within this model absorption will take place from S_0 to a state with energy $\hbar \omega_a$ above S_1, while normal fluorescence will occur between S_1 and a state with energy $S_0 + \hbar \omega_a$. Mirror image relationship holds, too. However some molecules do not show this relationship, as pyrene [6], which can be only accounted for by assuming a departure from Born - Oppenheimer approximation [6, 7].

Although "anomalous" fluorescence had been formerly assigned to $S_2 \rightarrow S_0$ transitions as in 1-12 - benzperylene [8], the fact that it is not a mirror image of $S_0 \rightarrow S_2$ absorption, (as might be expected since this is an allowed transition), together with the different behaviour with respect to temperature (shift and intensity) revealed that it indeed occurs from those vibronic states of S_1 where to absorption from S_0 occurs [9, 10]. This fluorescence is therefore known as "hot" fluorescence. When the first absorption band is hidden under the second, "hot" fluorescence can be recognized as it occurs at an energy $\hbar \omega_a$ above the $S_1 \rightarrow S_0$ energy gap exactly equal to the energy below $S_1 \rightarrow S_0$ at which "normal" fluorescence from a vibronic peak occurs.

"Hot" fluorescence gives, therefore, important information regarding radiationless processes in excited molecules and the nature of vibronic states. Using two-photon spectroscopy the mode selectivity in radiationless relaxation has been shown [11]. Most of the work has been carried in the gas phase where the molecule can be considered as isolated during the lifetime of the excited state; however the condensed phase spectra give information about the mechanism of vibronic mixing.

In the present work a study of the fluorescence of 1-12 - benzperylene in solution is made and the analysis of spectra at 77 K and 293 K provides an estimate of the rates of vibrational redistribution of the energy of the mixing modes, being shown to be rather slower than for pure vibrational states. From the ratio of intensities of "hot" and the corresponding "normal" peaks it can be shown that Herzberg - Teller treatment cannot be used and an alternative model, taking into account the departure from Born - Oppenheimer approximation is used, under some simplifying assumptions that allow numerical estimates.

2 — EXPERIMENTAL RESULTS

A solution of 5×10^{-6} M of 1-12 - benzperylene in 3 - methylpentane was used to study the fluorescence: it was excited at 27.400 cm^{-1} by a Xe lamp whose light was dispersed by a Hilger - Watts monochromator; it was viewed at right angles, through a Hilger - Watts single monochromator, blazed at 500 nm, by an EMI AVP 56 fast rise time photomultiplier. The detection was made by a Brookdeal lock-in amplifier, and corrected for fluctuations in the lamp by sending the signal as numerator in a home built ratiometer, the denominator originating in a small fraction of the light incident on the sample, converted into a fixed wavelength by means of a standard solution of Rhodamine - B. The spectra were further corrected for the wavelength dependent response of the monochromator and photomultiplier.

Corrected fluorescence spectra of 1-12 - benzperylene are shown in Fig. 1 and 2 (77 K and room temperature). It is only on higher gain that at 77 K a very low intensity fluorescence is observed at energies above the $S_1 \rightarrow S_0$ transition. At room temperature it becomes much stronger, in accordance with former results [8].

From the 77 K spectrum an analysis was made assuming a gaussian shape for each peak with a half width of 120 cm^{-1}. As anomalous fluorescence is practically absent, this spectrum gives the structure of the normal fluorescence band.

Besides the $S_1 \rightarrow S_0$ transition (24.700 cm^{-1}) there are four vibronic bands occurring at energies 260 cm^{-1} (B), 530 cm^{-1} (C), 800 cm^{-1} (D) and 1060 cm^{-1} (E) below $S_1 \rightarrow S_0$. The infrared spectrum shows peaks at energies close to the energies of these modes. A 4.2 K spectrum [12], also points to the existence of vibronic bands with energies close to these ones, clearly originating in non-symmetrical modes. All of these peaks show the characteristic 1400 cm^{-1} progression. It can be noted that the relative intensity of the last term of the symmetrical progression to that of the origin is higher for the pure electronic transition than for the vibronic bands, which can be due to a mixing of S_1 with S_3, as the symmetries of these states allow a mixing with the assistance of a symmetrical mode.

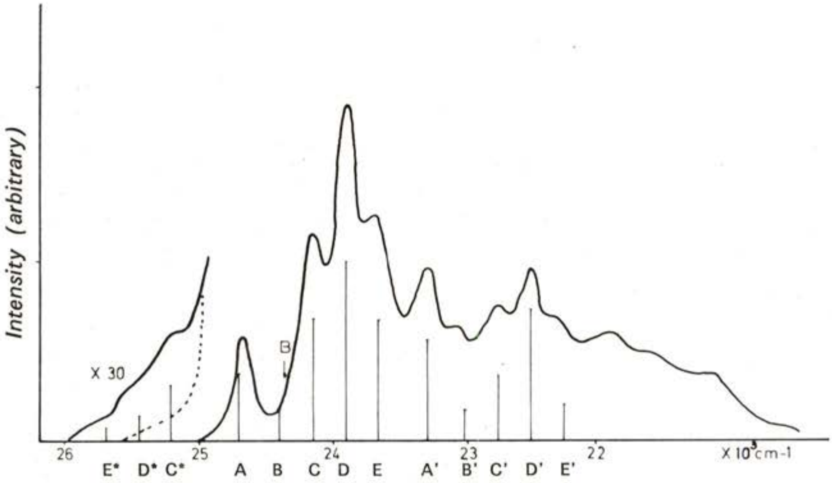

Fig. 1 — Emission spectrum (corrected) of 1-12 Benzperylene at 77 K. The lines show the location and relative intensity of the transitions referred in the text. A', B', C', D', E' are the 1400 cm^{-1} progression of A, B, C, D, E.

A similar analysis of the room temperature spectrum with a gaussian half-width of 240 cm^{-1} shows, together with a very similar behaviour of the "normal" fluorescence, the increase in the "anomalous" fluorescence, peaks being detected at energies 260 cm^{-1} (B*), 530 cm^{-1} (C*), 800 cm^{-1} (D*) and 1060 cm^{-1} (E*) above $S_1 \rightarrow S_0$, each one being origin of 1400 cm^{-1} vibrational

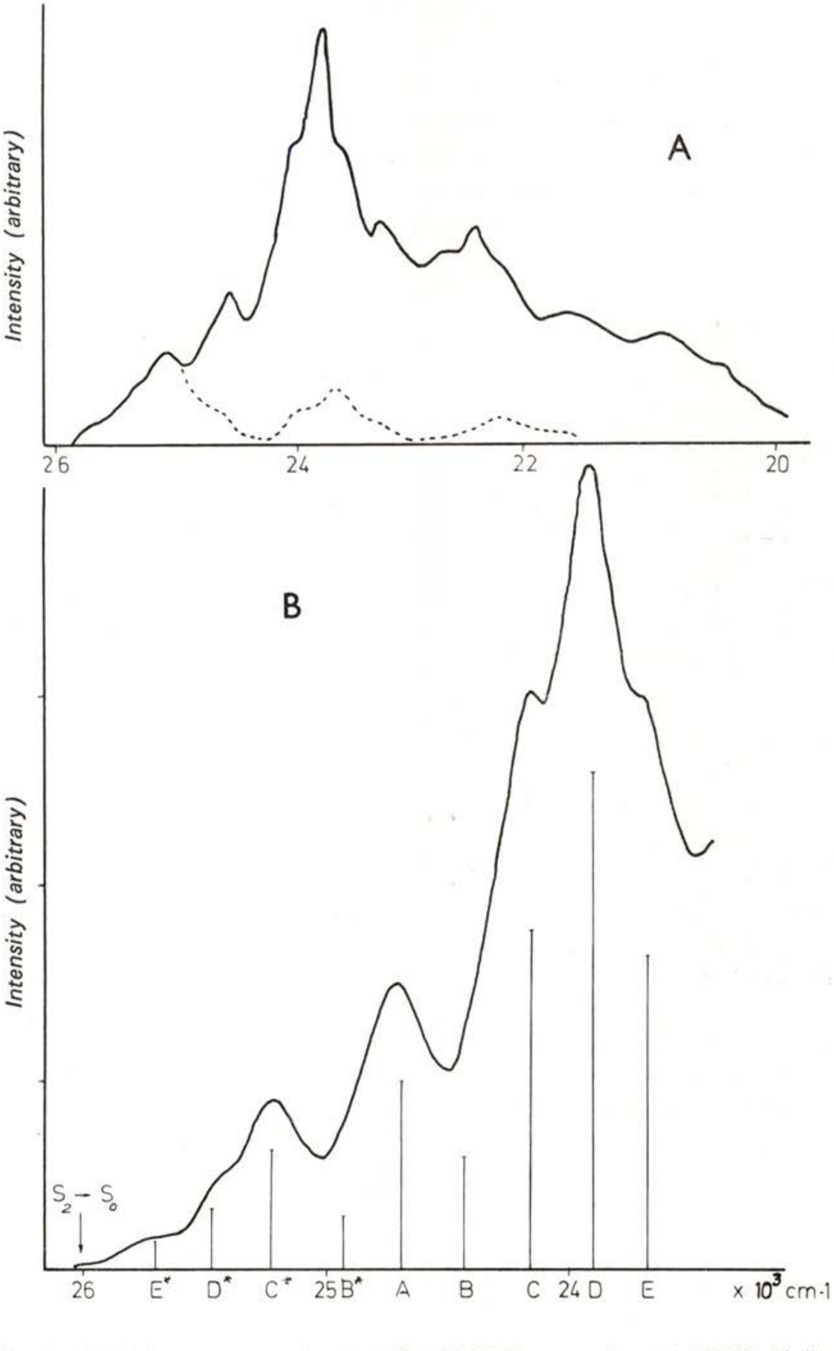

Fig. 2 — Emission spectrum (corrected) of 1-12 Benzperylene at 293 K. A) Dashed curve – "hot" fluorescence spectrum. B) Detail of the higher energy part of the spectrum, with relative intensities of "hot" and normal transitions.

progressions. A summary of the results is shown in Table 1. Assuming also that the vibrational progressions of the "hot" bands are similar to those of the corresponding "normal" bands, an estimate of the whole "hot" fluorescence can be made (Fig. 2A, dashed line).

TABLE 1

		A	B	B*	C	C*	D	D*	E	E*	F
Energy (cm^{-1})		24.700 (S_1-S_0)	24.700 - 260	24.700 + 260	24.700 - 530	24.700 + 530	24.700 - 800	24.700 + 800	24.700 - 1060	24.700 + 1060	26.120 (S_2-S_0)
Intensity	77 K	10.0	5.3	—	18.8	—	26.3	—	18.0	—	—
	293 K	10.0	6.1	2.7	18.7	6.6	26.0	3.5	18.5	2.0	0.5

3 — DISCUSSION

The states B*, C*, D* and E* are mainly thermally populated, the contribution of $S_2 \rightarrow S_0$ emission (F) being weak enough, at all temperatures, to be neglected in our analysis. In a former work [8], an activation energy of 690 cm^{-1} was found, but no attempt was made to distinguish between the behaviour of the different modes.

The 77 K spectrum allows us to estimate the fluorescence originating in states reached directly after excitation, since at this temperature, for instance, only 4.5×10^{-5} of the molecules in S_1 will have an energy 530 cm^{-1} above S_1, by thermal population. On the other hand, the room temperature spectrum shows mainly the contribution of thermally populated states.

3.1 — *Rate of vibrational redistribution of energy of the "hot" states*

The almost absence of $S_2 \rightarrow S_0$ fluorescence clearly shows that the rate of internal conversion from S_2 to S_1 is much faster than the rate of fluorescence from S_2 ; therefore internal conversion can be regarded as an irreversible process.

In this instance, after internal conversion a very fast energy loss to the solvent takes place and the molecule ends up in a vibronic state. In Fig. 3 the processes originating in this vibronic state are indicated. It is known that the rates of fluorescence from $S_1(k_{fl})$, of intersystem crossing (k_{ISC}) and internal conversion to $S_0(k_{IC})$ are temperature independent [13]. Assuming they are of the same order of magnitude for "hot" and "normal" states, under steady state conditions a relationship between concentrations of S_1 and S_1^* can be found, from which a ratio of "hot" (ϕ^*) and "normal" (ϕ) fluorescence can be obtained:

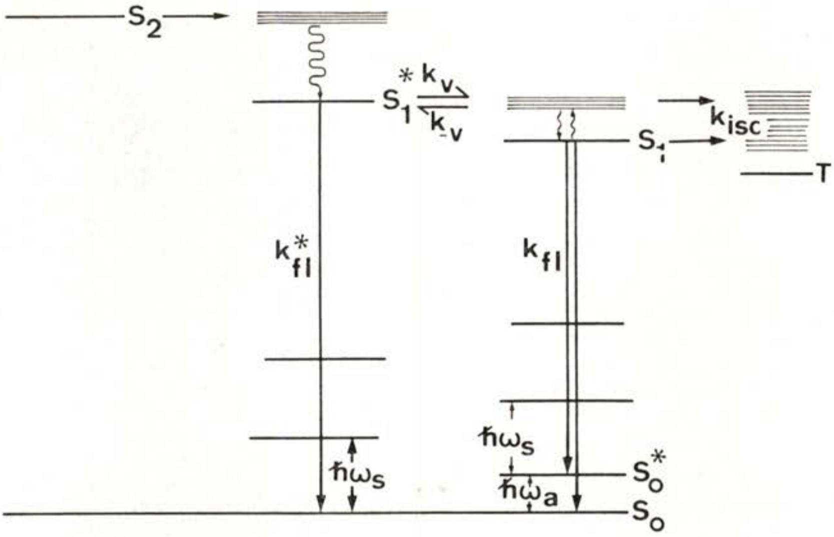

Fig. 3 — Schematic diagram of processes taking place after excitation. $(\hbar\,\omega_s = 1400\ \text{cm}^{-1})$.

$$\phi^* / \phi = (k_{fl}^* / k_{fl})\ k_{-v} / k_v + (k_{fl}^* / k_{fl}).\ \tau^{-1} \cdot k_v^{-1} \qquad (1)$$

with $\tau = (k_{fl} + k_{ISC} + k_{IC})^{-1}$

From the previous discussion, it can be seen that the first term on the right hand side of (1) dominates at room temperature while the second dominates at 77 K. The rate k_{-v} as thermal activation originates in interaction with the solvent, must be temperature dependent; therefore:

$$k_{-v} / k_v = \exp (- \hbar \omega / k T)$$

Due to the low intensity of fluorescence from the states with energy 260 cm^{-1} and 1060 cm^{-1} above S_1, only the other two will be considered.

The calculated values are presented in Table 2, using $\tau = 1,2 \times 10^{-7}$ s [8].

TABLE 2

Origin of Band	(ϕ^* / ϕ) 293 K	k_{fl}^* / k_{fl}	$\phi^*_{77} / \phi^*_{293}$	k_v (s^{-1})
C *	0.1	1.3	3×10^{-3}	2×10^9
D *	0.03	1.5	1.5×10^{-3}	6.5×10^9

The vibronic character of the "hot" states is clearly apparent from the slow rate of redistribution of the vibrational energy of the active modes, when compared with the same rate of a pure vibrational mode in solution (of the order of 10^{11} s^{-1}).

3.2 — *Comparison between intensity of "hot" and "normal" peaks and theoretical calculations*

It is possible to calculate the ratio of Einstein's B coefficients for "hot" and corresponding "normal" peaks directly from the experimental values of peak intensities at room temperature. As at this temperature the "hot" state is dominantly thermally populated, and under the assumption that the rates of intersystem crossing and internal conversion from the "hot" states are of similar order of magnitude as from "normal" states, the ratio B* / B ("hot" / "normal") will be:

$$B^* / B = (I^* / I) \left(\frac{E_1 - \hbar\omega}{E_1 + \hbar\omega} \right)^3 \exp(\hbar\omega / kT)$$

The results obtained from the measured intensities are presented in Table 3. They clearly deviate from the Herzberg - Teller model, that predicts a ratio of 1 for the two corresponding peaks.

TABLE 3

$\hbar\omega$	260	530	800	1060
B * / B Exp. results	1.5	4.1	5.5	16.6
B * / B Calculated	2.1	4.8	12.8	46.9

This clearly points to the fact that electrons do not follow instantaneously the nuclear motion, and a breakdown of Born - Oppenheimer approximation has to be taken into account.

In the present calculation, based on previous results [6], a simpler model is used, with the following simplifying assumptions:

I — Interactions occur only between S_1 and S_2, $S_2 \rightarrow S_0$ being symmetry allowed and $S_1 \rightarrow S_0$ symmetry forbidden.

II — The vibrational modes of the molecules behave like harmonic oscillators, with the same frequencies in S_0, S_1 and S_2.

III — Only one symmetrical mode shows transitions from S_0 to S_1 and S_2.

IV — The translation of this mode is the same in S_1 and S_2.

V — The modes active in the mixing are uncoupled, with coordinate Q_a, wave function χ_a and energies $\hbar\omega_a$.

The operator that accounts for the breakdown of the Born - Oppenheimer approximation mixes S_1 and S_2, one state with the vibrational active mode in its ground level and the other in the first excited state, due to the term of the breakdown operator $\partial / \partial Q_a$ that acts on χ_a [6].

Labelling the unperturbed wave function (adiabatic Born-Oppenheimer) with two indexes, the first referring to the electronic part and the second to the vibrational part of the wave function, the mixing occurs between $\psi_{1,1}$ and $\psi_{2,0}$ in absorption or "hot" emission, and between $\psi_{1,0}$ and $\psi_{2,1}$ in "normal" fluorescence.

Therefore the mixing states are separated by $E_2 - E_1 - \hbar \omega_a$ and $E_2 - E_1 + \hbar \omega_a$ respectively.

Because it is only the S_2 character of the vibronic states that accounts for the transition dipole moment between those states and S_0, their ratio will be:

$$M_{0 \to 1} / M_{1 \to 0} = (E_2 - E_1 - \hbar \omega_a) / (E_2 - E_1 + \hbar \omega_a)$$

and therefore:

$$B^* / B = [(E_2 - E_1 - \hbar \omega_a) / (E_2 - E_1 + \hbar \omega_a)]^2 \qquad (2)$$

Equation (2) provides a straightforward means of calculating the ratio B* / B for the different vibronic states. The results are shown in Table 3.

The agreement with experiment is fair in the lower energy states, but deviates for the other two.

Some causes may account for this fact: If hypothesis IV is not satisfied, that is, if the translation of the symmetrical mode is not the same for S_1 and S_2 then a mixing of S_1 with S_2 with the 1400 cm^{-1} mode in its first excited level is possible, as the vibrational wave functions of this mode in the two states will no longer belong to the same orthonormal set. This effect will be larger for the higher energy mixing modes as the ratio will now be given by $(E_2 + 1400) - E_1 \pm \hbar \omega_a$.

However to get agreement with experiment it would have to be assumed a larger contribution of this term than the previously considered one, which is unlikely as the symmetrical progressions do not differ much for $S_0 \to S_2$ absorption and $S_1 \to S_0$ vibronic emission.

Another reason for the experimental ratios being smaller than the theoretical ones can be the fact that $S_1 \to S_0$ is not totally forbidden as assumed in I. Therefore some of the molecules in a vibronic state (S_1^*) can decay to a ground state with the mixing mode in its first excited level, that is, at an energy corresponding to the A transition. This accounts for a decreased intensity in the "hot" fluorescence from the vibronic states. The weaker the vibronic mixing, the more pronounced is this effect on the measured ratios.

The spectrum however shows that the 800 cm^{-1} mode is the one that gives the higher intensity of fluorescence so the mixing is strong, for this mode. Obviously this effect can not account for the results.

On the other hand the experimental values of the ratios for the B coefficients from spectra in the gas phase [14] are closer to the calculated ratios.

It seems more likely that the ratio of intersystem crossing from the higher vibronic states is larger than for the other states.

This will be possible if there is a triplet state close in energy with $E_1 + 800\ cm^{-1}$, to which intersystem crossing is possible, likely T_2 ($E_1 + 800\ cm^{-1}$ and $E_1 + 1060\ cm^{-1}$ are 620 cm^{-1} and 360 cm^{-1}, respectively, below S_2). In the gas phase the energy gap between S_1 and S_2 is larger, and so the vibronic levels will be all below T_2 ; so the rate of intersystem crossing will be again of similar order of magnitude for all states, and so the experimental results are again closer to the theoretical values.

4 — SUMMARY

1-12 benzperylene is a molecule with an electronic structure that renders "hot" fluorescence a likely process. The analysis of the fluorescence spectrum both at room temperature and at 77 K (therefore in condensed phase) makes it possible to estimate the rate of vibrational redistribution of the energy of the vibronic states, that are rather larger than usually found for vibrational modes. Although the first absorption band is hidden under the second it can be shown from the ratio of intensities of "hot" and "normal" corresponding peaks, that the Born - Oppenheimer approximation does not hold. A perturbation method based on the departure from this approximation gives ratios in fair agreement with experiment.

This work owes much to a former collaboration with the late G. J. Hoytink. Helpful comments of Dr. M. F. Thomaz are gratefully acknowledged.

REFERENCES

[1] D. HUPPERT, J. JORTNER, P. M. RENTZEPIS, *J. Chem. Phys.* **56**, 4826 (1972).

[2] M. KASHA, *Disc. Far. Soc.* **9**, 14 (1950).

[3] P. A. GELDOF, R. P. H. RETTSCHNICK and G. J. HOYTINK, *Chem. Phys. Lett.* **4**, 59 (1969).

[4] J. B. BIRKS, *Inorganic Molecular Photophysics* vol. 2, pg. 453 (Wiley, 1975).

[5] G. HERZBERG, and I. TELLER, *Z. Physik. Chem.* **B21**, 410 (1933).

[6] P. A. GELDOF, R. P. H. RETTSCHNICK and G. J. HOYTINK, *Chem. Phys. Lett.* **10**, 549 (1971).

[7] G. ORLANDI, *Chem. Phys. Lett.* **19**, 459 (1973).

[8] J. G. CARTER, L. G. CHRISTOPHOROU and C. E. EASTERLY, *J. Chem. Soc Farad. Trans.* **69**, 471 (1973).

[9] G. J. HOYTINK, *Chem. Phys. Lett.* **26**, 16 (1974).

[10] G. J. HOYTINK, *Chem. Phys. Lett.* **22**, 10 (1973).

[11] H. B. LIN, M. R. TOPP, *Chem. Phys. Lett.* **67**, 273 (1979).

[12] K. OHNO, *Chem. Phys. Lett.* **70**, 526 (1980).

[13] V. R. DAWSON, J. L. KROPP, *J. Chem. Phys.* **73**, 1752 (1969).

[14] M. ESTELA PEREIRA, To be published.