Rotationally resolved laser spectroscopy of tetracene and its van der Waals complexes with inert gas atoms

W. M. van Herpen, W. Leo Meerts, and A. Dymanus
Fysisch Laboratorium, Katholieke Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 10 December 1986; accepted 24 February 1987)

By using a molecular beam apparatus in combination with a single frequency dye laser we were able to resolve several rovibronic bands in the S_1 electronic state of tetracene ($C_{18}H_{12}$) and its van der Waals complexes with inert gas atoms. The spectra of tetracene have been assigned and rotational constants were derived for the S_0 and S_1 electronic state. The existence of perturbations in the rotational spectra of the van der Waals complexes is demonstrated.

I. INTRODUCTION

The study of the structure, binding energies and dynamic behavior of large (e.g., aromatic) molecules and their van der Waals (vdW) complexes is hindered by complicated spectra. One can try to use Doppler-free techniques in cell experiments[1] but then the relatively high temperature gives rise to an enormous amount of spectral lines in the rotational bands. An experimental setup with a free jet expansion of the molecules in a seeding gas is more convenient. In this way, a cooling of the internal degrees of freedom of the molecules is accomplished, resulting in a considerable reduction of the number of spectral lines. Moreover, vdW complexes are readily formed in the expansion. If laser excitation occurs directly behind the nozzle the spectral resolution is sufficient to study rotational bands of smaller molecules like the benzene–helium vdW complex,[2] but for larger molecules like anthracene,[3] tetracene,[4] and pentacene,[5] only vibrational resolution is achieved. By enlarging the distance between the nozzle and excitation area of the crossing laser beam and by strongly collimating the molecular beam, one can reduce the residual Doppler width. With the latter setup and using a single frequency laser, we were able to resolve rotational spectra of naphthalene,[6] the fluorene–argon vdW complex,[7] and even the molecular eigenstates of pyrazine.[8]

We report the study of rovibronic bands of tetracene (T) and its vdW complexes with rare gas (R) atoms, argon, krypton, and xenon, in the regime of low vibrational energy ($< 500\ \mathrm{cm}^{-1}$). A preliminary report of some of these results has already been presented.[9] In the present paper, a full account of the available information is given. The tetracene molecule consists of four benzene rings in line. The S_1 state of T has only been studied with vibrational resolution.[4] It is therefore necessary to study rotational resolved spectra of the molecule before proceeding to vdW complexes. The rotational bands give insight in the structure of the free molecule and they also serve as a check for the vibrational assignment. It was found before[4] that vibrational excitation in the S_1 state, $1600\ \mathrm{cm}^{-1}$ above the ground vibrational level, shows a shortening of the decay lifetime. This effect has been attributed either to the S_1–T intersystem crossing or to the S_1–S_0 internal conversion. A study at rotational resolution allows one to investigate such electronic interactions, even near the electronic origin of the S_1 state. It will be shown in this paper that such interstate couplings, although weak, show up in the regime of low vibrational energies. These effects are enhanced in the vdW complexes of T with noble gas atoms and are clearly observed in the present study. The increased interstate coupling is found to be in agreement with lifetime measurements at vibrational resolution,[11] where it is shown that the decay lifetime of the T–R complexes decreases rapidly in the order argon, krypton and xenon.

Model calculations[10] of the T–R vdW complexes predict a possibility of tunneling effects by a large amplitude motion of the rare gas atom. An experimental determination of the complex structure may serve as a test of the potential energy surface. For the T–R_2 molecules the existence of chemical isomers is theoretically unlikely. An experimental unambiguous determination of the structure is a worthwhile undertaking. It was found, however, that no rotationally resolved spectra for the higher clusters were observable. This lead to the conclusion that the interstate interactions with the S_1 state are increased in the larger clusters.

II. EXPERIMENTAL SETUP

In order to obtain much simpler (less congested) spectra we used the seeded beam technique. In this way considerable reduction of the internal temperature of molecules emerging in an expansion is acheived. Moreover, this expansion has the advantage of an efficient production of vdW complexes of T with the seeding gas in the molecular beam. The spectrometer has been described before.[6,12] We used a quartz source, in which a sample of T (Aldrich) was heated to approximately 210 °C. The vapor, mixed with the seeding gas, was expanded through a 100 μm nozzle into a vacuum chamber. The molecular beam was doubly skimmed, reducing the Doppler linewidth to about 15 MHz. The interaction zone with the laser was at 30 cm from the beam orifice. The undispersed laser-induced fluorescence was imaged onto the photocathode of a photomultiplier tube (EMI 9863/350). We used a standard photon counting system (Ortec Brookdeal 5C1). The molecular beam was chopped and phase sensitive detection was applied to suppress scattered laser light. The typical preset counting time was 0.1 s.

Narrow band radiation was obtained from a single frequency cw dye laser system (Coherent Radiation 599-21). A solution of stilbene 3 in ethylene glycol was used as a gain medium. The dye laser was pumped by the UV lines (351–364 nm) from an Ar-ion laser (Spectra Physics 171-UV).

0021-9606/87/130182-09$02.10

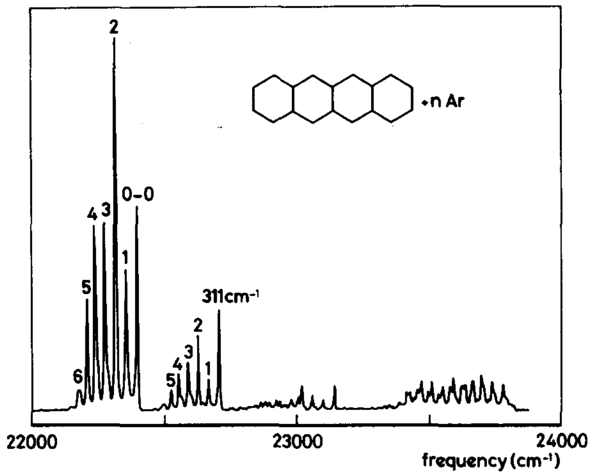

FIG. 1. Low resolution vibronic spectrum of tetracene seeded in argon (backing pressure 4 bar). The T–Ar$_n$ ($n = 1,2...$) vdW complexes are indicated. The spectrum has not been normalized to the laser intensity.

The bandwidth of the dye laser was about 3 MHz and the typical output power 50 mW. For relative frequency marking, we applied a sealed-off temperature stabilized Fabry–Perot interferometer with a 150 MHz free spectral range. For absolute frequency measurements a home-built wavelength meter was used.[12] Its principle is based on a Michelson interferometer which compares the dye laser wavelength with the accurately known wavelength of a reference HeNe laser. By removing the intracavity étalons of the dye laser, the bandwidth could be increased to 30 GHz. In that case, the laser could be continously scanned by a Lyot filter over the whole region of the gain medium.

The spectrometer is interfaced with a microcomputer (PDP11/23 plus). Data recording by the computer provides a large dynamic range in the spectra. The computer scans the laser and stores simultanously data from the spectrum and the frequency markers. In processing the data it becomes possible to make accurate corrections for nonlinearity in the scan. Moreover, the computer facilitates the tedious determination of the spectral positions and intensities.

III. THE $S_1 \leftarrow S_0$ TRANSITION OF TETRACENE

Excitation spectra at vibrational resolution in a seeded molecular beam are obscured by spectra of vdW complexes of T with seeding gas atoms. Distinction between the various transitions is based on the use of different seeding gases, the pressure dependence of the spectral intensities and the order of appearance of various bands belonging to the vdW complexes.[11,13,14] In Fig. 1, a typical low resolution spectrum of T expanded in argon is shown. Effective cooling of the internal temperature of the molecule is accomplished at lower pressures than formation of vdW complexes. These complexes appear at relatively high pressures and increase rapidly with the backing pressure. All vibronic transitions in our experiments arise from the vibrational ground state due to the effective vibrational cooling in the expansion. To identify the various complexes and vibrational states, it proved to be very helpful to operate our laser at low ($1\ \mathrm{cm}^{-1}$) resolution. This also allowed an easy optimalization of the backing pressure for the formation of different complexes.

Tetracene belongs to the D_{2h} point group and the ground and singly excited electronic states are characterized by A_g and B_{2u} symmetry (with the axis chosen as $\{x,y,z\} = \{c,b,a\}$). Several vibrational states of the $S_1 \leftarrow S_0$ transition of tetracene have been assigned by Amirav *et al.*[4] The vibrational structure of the S_1 state can be divided into three regimes. Below a vibrational energy (E_v) of $E_v = 1000$ cm^{-1} there is a sparse level structure. Above this level, Fermi resonances appear, fading into a quasicontinuum at about $E_v = 1800\ \mathrm{cm}^{-1}$. We studied three vibrational states in the low energy regime under rotational resolution. Two of these states belong to an a_g-type totally symmetric vibrational mode, which is active for the $S_1\ (^1B_{2u}) \leftarrow S_0\ (^1A_g)$ symmetry-allowed electronic transition. The nontotally symmetric b_{3g}-type mode, which has also been studied, gains its intensity from a coupling with the higher energy $^1B_{1u}$ electronic state and is much weaker than the symmetry allowed transitions. The observed transition frequencies to the excited state vibrational modes are listed in Table I.

The spectrum around 22 396.53(2) cm^{-1} was identified as the 0–0 electronic transition. Small differences in spectral positions do exist between different investigations.[11,14,15] We observed no spectral features at lower frequencies which were independent of the type of seeding gas. The spectrum appeared to be very strong. To avoid strong saturation effects, reduction of the cw laser power to a few mW was necessary at a focus of about 0.5 mm diam in the interaction region. The transition around 22 708 cm^{-1} belongs to a totally symmetric (311 cm^{-1}) vibrational mode in the excited electronic state. As expected, the spectrum thus proved to be of the same transition type as the 0–0 transition.

Within experimental accuracy, we did not observe any differences between the 0–0 and 311 cm^{-1} vibronic transition. The linewidth in the spectra is 15 MHz and is determined by the residual Doppler width of the spectrometer.

TABLE I. Experimental rotation-free $S_1\ (^1B_{2u}) \leftarrow S_0\ (^1A_g)$ vibronic transition frequencies ν_0 of tetracene and the relative shifts[a] ($\Delta\nu = \nu - \nu_0$) of the corresponding transitions of the vdW complexes.

Assignment	T ν_0 (cm^{-1})	T-Ar $\Delta\nu$ (cm^{-1})	T-Ar$_2$	T-Kr	T-Kr$_2$	T-Xe
(0–0)	22 396.53(2)	−41.67(5)	−80.6(1)	−66.9(1)	−124(1)	−110.0(1)
(311 cm^{-1})	22 707.84(2)	−41.42(5)	−79.9(1)	−66.5(1)	−123.4(1)	
(471 cm^{-1})	22 867.62(2)	−41.52(5)	−80.0(1)	−66.9(1)		

[a] The accuracy for the complexes is limited by the lack of a complete rotational assignment.

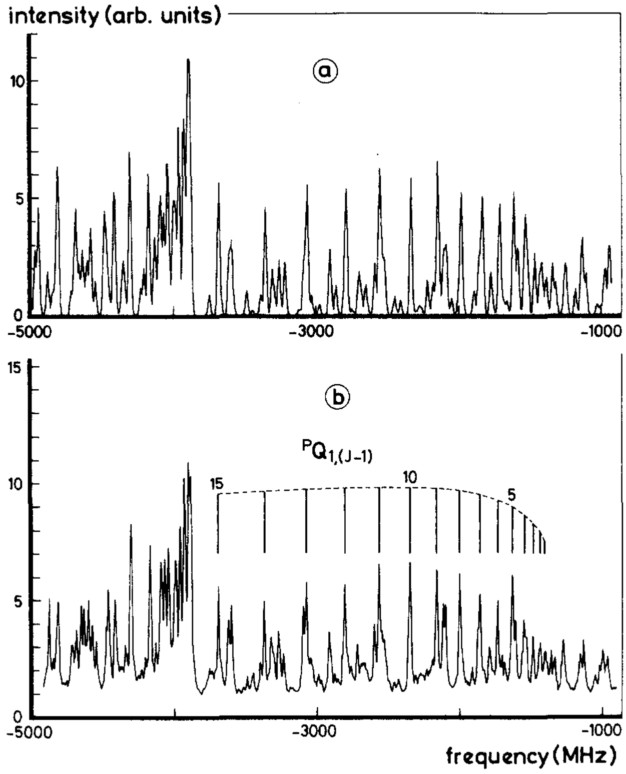

FIG. 2. Part of the 0–0 perpendicular band around $\nu_0 = 22\,396.53(2)$ cm^{-1} of tetracene. In the experimental spectrum (b) a Q branch with $K''_{-1} = 1$ is indicated. Band (a) is calculated from the obtained rotational constants, using rotational temperature of 2.3 K.

TABLE II. Rotational constants of the tetracene molecule in the S_0 (^1A_g) and S_1 ($^1B_{2u}$) electronic states ($\Delta A = A' - A''$, $\Delta B = B' - B''$, $\Delta C = C' - C''$). The data is derived from the 0–0 vibrationless and the 471 cm^{-1} vibrational transition.

S_0		S_1	
Constant	(MHz)	Constant	(MHz)
A	1630 (1)	ΔA	17.4(1.2)
B	213.4(2)	ΔB	− 1.81(8)
C	188.8(2)	ΔC	− 1.19(8)

This is in agreement with decay lifetime measurements of the excited state.[4] The spectra were uniquely identified as a b-type perpendicular transition. This corresponds to a transition dipole moment along the short molecular axis. The b-type transitions follow the selection rules ee↔oo and eo↔oe for $K''_{-1},K''_1 \leftrightarrow K'_{-1},K'_1$. Such a spectrum shows hardly any characteristic features and it consists of complicated subbands. Part of the 0–0 transition is depicted in Fig. 2. A Q band with $K''_{-1} = 1$ is indicated. As a starting point for the assignment, we used rotational constants derived for the 471 cm^{-1} vibronic transition which will be discussed below. A total of 65 lines of this spectrum in a 10 GHz region around the origin was fitted to an asymmetric rotor model.[16–18] All strong spectral lines in this region were included, containing rotational states up to $J = 15$. From the fit we obtain the rotation-free transition frequency ν_0 and the A, B, and C rotational constants in the excited state as well as the ground electronic state. In the final fit, all parameters were varied simultaneously with an excellent result. A standard deviation of 2.2 MHz was obtained. None of the observed frequencies deviated more than 5 MHz from the calculated value. The spectral intensities were considered separately and will be discussed below. As will be shown, not only the frequencies, but also the intensities of the spectral lines could be accounted for. The molecular constants are given in Table II. These constants are in good agreement with those derived from crystallographic data.[19,20] All data could be fitted very well within experimental accuracy without taking distortion effects into account. Also, it can be easily deduced from the rotational constants that there is no significant inertial defect ΔI in the T molecule in neither the ground state nor the studied excited states.

The observed 471 cm^{-1} vibrational mode (Fig. 3) corresponds to a nontotally symmetric b_{3g}-type vibration. The rovibronic spectrum was identified as an a-type parallel band with selection rules ee↔eo and oo↔oe for $K''_{-1},K''_1 \leftrightarrow K'_{-1},K'_1$. This spectrum shows a characteristic P, Q, and R branch. Moreover, the density of lines is less than in the perpendicular bands, so the identification of the spectrum is much simplified. As a starting point for the assignment, we used estimated rotational constants, derived from the crystal structure. We assigned a total of 160 lines in an 8 GHz region around the band origin and fitted them to the asymmetric rotor model. Even part of the Q branch was resolved and could be included in the fit. All parameters were varied simultaneously and this fit also proved very satisfactory with a standard deviation of 4.0 MHz. All data could be fitted within experimental accuracy. The rotational constants derived conformed to the 0–0 transition within statistical uncertainty. The values listed in Table II stem from combined data of both spectra.

For the parallel-type spectrum, we observed a number of single rotational transitions which allowed us to determine the rotational temperature of molecules in the beam. The intensity of separate rovibronic lines is given by

$$I = I_0(2J+1)g_n A(J'',K''_{-1},K''_1) \times \exp\left[-\frac{E(J'',K''_{-1},K''_1)}{kT_{\mathrm{rot}}}\right]. \qquad (1)$$

Herein, I_0 is a constant and $E(J'',K''_{-1},K''_1)$ the rotational energy of the ground state level. As T is a near prolate asymmetric top $A(J'',K''_{-1},K''_1)$ can be approximated by the Hönl–London factors for the limiting case of a symmetric top molecule. The factor g_n is the statistical weight of the nuclear spin, determined by the number of allowed spin configurations. The T molecule can be characterized by D_{2h} molecular symmetry. It contains three groups of four equivalent hydrogen nuclear spins each. The value for g_n is 1072 for $(K''_{-1},K''_1) = (\mathrm{e,e})$ and 1008 in all other cases. The statistical weights are very close for the different rotational symmetries because of the large number of hydrogen atoms in the molecule. Such a small difference is below our detection limit and can be neglected. Relative intensities from the 471 cm^{-1} parallel band were fitted to Eq. (1). The spectrum was taken at a typical backing pressure of 2 bar, using argon

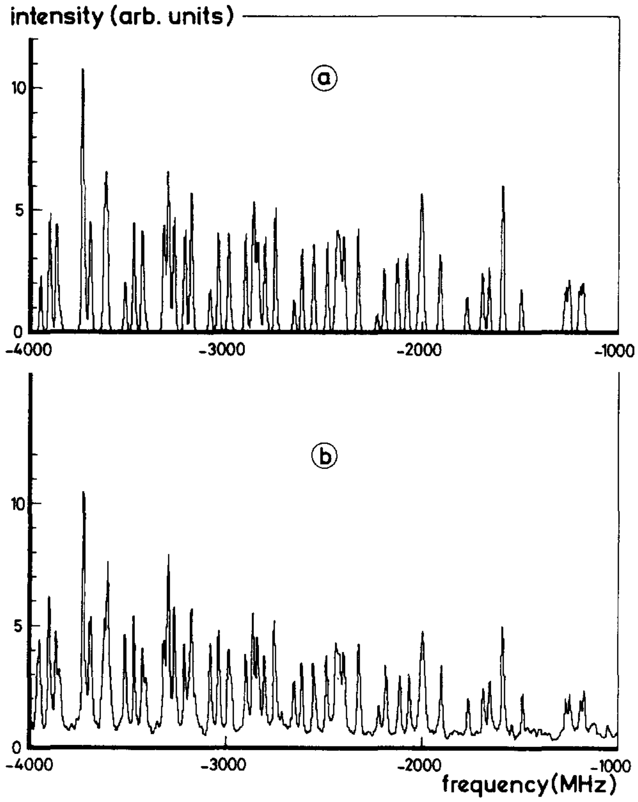

FIG. 3. Part of the P branch of the 471 cm^{-1} parallel band of tetracene around $\nu_0 = 22\,867.62(2)$ cm^{-1}. The experimental (b) as well as the calculated (a) spectrum is reproduced.

for a seeding gas. A single rotational temperature $T_{\mathrm{rot}} = 2.3(3)$ K could be assigned.

By simulation of the spectra using Eq. (1) and the constants derived (Figs. 2 and 3) it appeared that there were no strong unidentified spectral features in either the parallel or the perpendicular bands. The lack of significant inertia defect and distortion effects, indicates the planar rigid structure of this molecule in the ground state, as well as the lower vibrational modes of the S_1 electronic state. The vibrational states of T considered in this work all showed clear unperturbed rotational spectra. Similar data in the low energy regime of benzene[1] and naphthalene[6] also show that these molecules exhibit no observable centrifugal distortion and have a small inertial defect in the ground state as well as the first excited electronic state. At higher vibrational energy, the rotational spectra experience perturbations from e.g., Coriolis couplings between vibrational states[21] or Fermi resonances. For the anthracene molecule, no rotational resolved spectra are available. Rotational contour analysis[3] tend to the conclusion that, in the low energy regime, perturbations are not very large. These spectra of aromatic molecules are thus different from those of e.g., azabenzenes as pyrazine,[8] pyrimidine,[22] and triazine,[23] which show perturbations due to intramolecular couplings, also at low vibrational modes.

The linewidth in the spectra does not exceed the residual Doppler width in the spectrometer. The experimental error in the intensities is at least 5% and shows no significant deviation from the expected values according to Eq. (1). As can be seen from Figs. 2 and 3, we observed a significant background in the spectra of T in the order of 20% of the intensity of single lines. This constant level cannot be caused by laser stray light, because the molecular beam was chopped and phase sensitive detection was applied. Such a background was absent in earlier measurements on the IO radical[12] where the same apparatus was used and is apparently not due to some machine effect. The overlap of spectral lines is limited, certainly in the parallel band, and thus cannot account for the background signal. As possible explanations for this signal, we will discuss the contribution from isotopic species and interstate couplings.

The natural abundance of the ^{13}C isotope is about 1%. Since there are 18 carbon atoms in tetracene about 19% of the T molecules will contain one or more ^{13}C atom. Not all carbon atoms are at equivalent positions and consequently not all isotope bands will coincide. Nevertheless, we did not observe separate transitions due to isotropic species of T. The many different isotopic species might give rise to an almost constant background in the spectra due to overlap of lines. The intensity of this level depends on the size of the relative shift of the different isotope bands and is hard to estimate. However, the contributions from isotopic species might in part explain the background.

Although we assign a "clean" rotational spectrum in T, in contrast to observations in pyrazine[8] and pyrimidine,[22] it is not excluded that weak couplings between the S_1 state and other states in the molecule give rise to the observed background signal. Our observations in azabenzenes justify the assumption that a sizable fraction of the rotational lines in T is accompanied by weak satellite transitions due to either intersystem crossings, i.e., singlet–triplet interactions, or internal conversion, S_1–S' couplings. Because of the very high density of rotational lines in T, we might expect a complete overlap of these weak transitions, resulting in a smooth background. This speculation is supported by the experimental results on the tetracene–noble gas complexes presented in the next section. In that case, the spectra indicate a strong increase in coupling between the S_1 and other states in conjuction with a strong increase of the smooth background signal.

IV. TETRACENE–RARE GAS VAN DER WAALS COMPLEXES

A. Formation and identification

We studied T–R$_n$ (R = Ar,Kr,Xe; $n = 1,2$) vdW complexes in the molecular beam under rotational resolution. These complexes are effectively formed in the expansion of T with the rare gas. The production of T–He$_n$ and T–Ne$_n$ complexes in this way proved unsuccessful. Even at the maximum backing pressure of 4 bar the cooling in the expansion was insufficient. At this pressure, the cooling with neon is much better than with helium as carrier gas. Amirav *et al.*[11] claimed the observation of the weak 0–0 band of the T–Ne complex, using a high backing pressure. This band is shifted − 5 cm^{-1} with respect to the 0–0 transition in T. Due to the vibrational congestion in our spectra, we were unable to probe this region under rotational resolution. Mixtures of a small amount of helium or neon in argon improved the cooling conditions but were too inefficient in formation of the T–

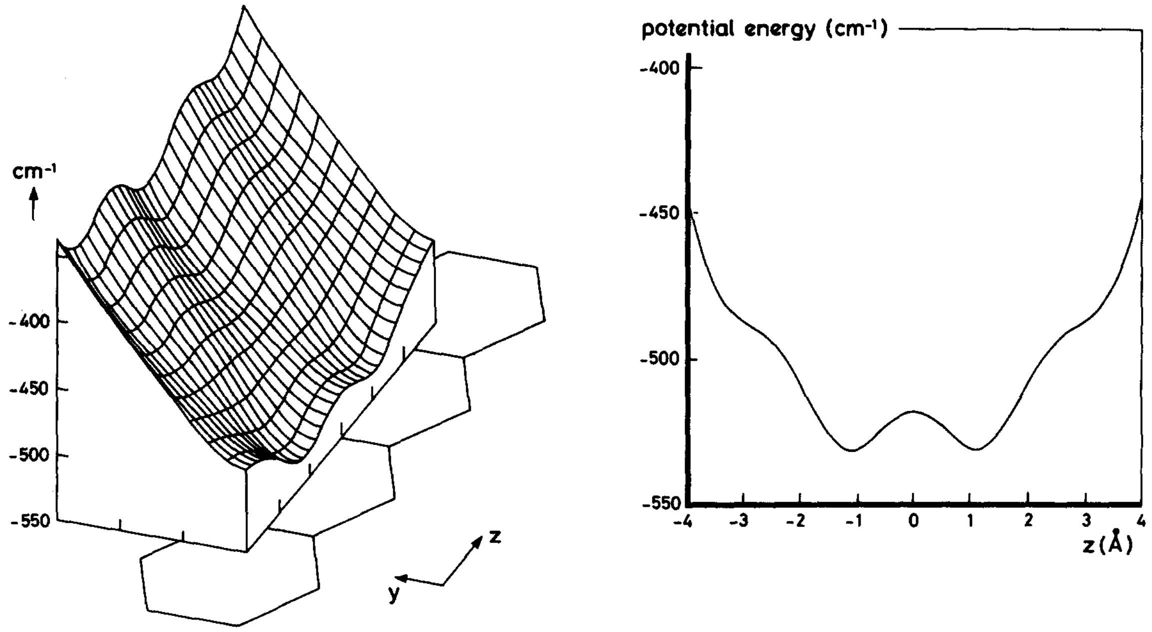

FIG. 4. Calculated energy surface of the tetracene–argon interaction. The skeleton of the tetracene molecule is shown on the same scale and with the same orientation as used for the surface. The potential along the z axis at $y = 0$ clearly shows a double well structure.

He or T–Ne vdW complexes. On the basis of former experience[7] we expect the rotational temperature of the T–R_n complexes in the argon beam to be comparable to that of the host molecule. Internal heating in complex formation is effectively cooled in the molecular expansion using argon, krypton, or xenon.

The vibrational assignment of various T–R_n transitions has been reported by Amirav *et al.*[11] The accuracy in their absolute frequencies is limited [14,15] by nonlinearity in the scans. We studied transitions in the T–R_n complexes corresponding to the transitions in the T molecule mentioned before (i.e., the 0–0 vibrationless, 311 and 471 cm^{-1} vibrational transitions). In Fig. 1, a low resolution spectrum is depicted of T expanded in argon at a backing pressure of 4 bar. The various bands are well separated. Transitions in the various complexes are more or less regularly shifted with respect to corresponding bands in the parent molecule. The vibrational excitations of the T–R_n molecules are very close but not identical to those of T, indicating that the vibrational mode of the complex is based in large part upon the vibration of the T host molecule. The spectra are red shifted with respect to the analogous transitions in the parent molecule. There is no spectral overlap between the various transitions of T and the different complexes in the regime of low vibrational energy. For the T–Kr_n and T–Xe_n complexes, we observed spectra similar to that of Fig. 1 but with some extra weak spectral features which were assigned as vdW vibrational modes of the complexes. This structure is well resolved but of such low intensity that it was not further explored.

B. Theoretical considerations

Model calculations of T–R_n complexes have been performed by Ondrechen *et al.*[10] A Lennard-Jones 6-12 potential was used with pairwise interactions between the R atom and atoms in the T molecule. Higher order terms and three-body interactions were neglected. We repeated the model calculations with a slight modification but extended the calculated area of the potential surface over the entire molecule. The main goal was to thoroughly examine the possible existence of chemical isomers. Although these calculations provide only a rough indication of the geometry of the complexes, we found similar calculations very satisfactory for the fluorene–argon vdW complex.[7] In Fig. 4, part of the T–Ar potential surface is shown. We used for the interaction energy

$$V_{\text{T-R}} = -\sum_{\alpha} \frac{A_{\text{R}\alpha}}{r_{\text{R}\alpha}^6}\left(1-\frac{r_0^6}{r_{\text{R}\alpha}^6}\right), \qquad (2)$$

where the coefficients $A_{\text{R}\alpha}$ and r_0 are obtained from Ref. 10. The summation is over all atoms in the T host molecule at a distance $r_{\text{R}\alpha}$ of the rare gas atom. We varied the distance of the R atom to the molecular plane for minimum energy. This modification to Ref. 10 was certainly necessary in the case of nonplanar molecules like fluorene although it does not affect the results for T very much. A favorable position of a single R atom is predicted above the T molecular plane, near the center of an inner ring of the molecule. The calculated distance between the inert gas atom and the molecular plane is 3.43, 3.50, and 3.72 Å for argon, krypton, and xenon, respectively. In spite of the simplicity of the model, the calculations rule out the existence of any other configuration of the T–R complex. The unique equilibrium structure of the complexes in principal can be determined from rotationally resolved spectra of the T–R complex and the T parent molecule. This provides direct information on the potential surface.

The T–R theoretical potential surface has a kind of double well shape along the long molecular axis, which becomes more pronounced for smaller noble gas atoms. Depending

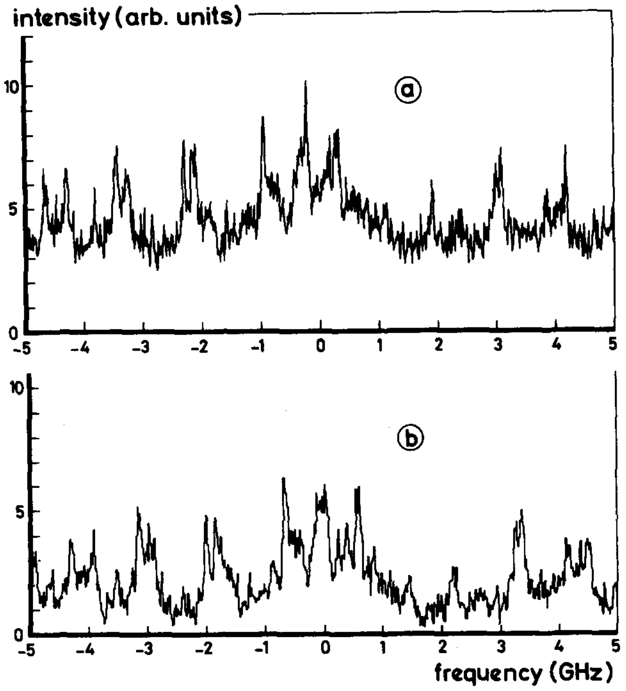

FIG. 5. Comparison between the 0–0 (b) and 311 cm^{-1} (a) rovibronic bands of the tetracene–argon vdW complex.

on the height of the barrier (estimated 14 cm^{-1} for T–Ar), this will give rise to tunneling splitting, resulting in doubling of the rotational spectra. Calculations of such vdW vibrational modes have been reported for the pentacene–R complexes.[24] As is clear from Fig. 4, the potential surface is rather flat along the long molecular axis. A large amplitude motion of the R atom along this axis might thus be possible. Let us consider such a large amplitude motion (contortion)[25] of the R atom along the T long molecular axis. If the separation of this motion and rotation is assumed, the zero-order roconvibronic wave functions are of the form

$$\Phi_{\rm rcve} = \Phi_{\rm rot}\,\Phi_{\rm con}\,\Phi_{\rm vib}\,\Phi_{\rm el} \tag{3}$$

We describe the T–R complex by C_{2v} symmetry and assume that the symmetries of the wave functions of the T parent molecule are more or less conserved in the T–R complex. It then follows that allowed electronic–contortional transitions are determined by the condition for the irreducible representations

$$\Gamma(\Phi'_{\rm con}\,\Phi'_{\rm el}) \otimes [\Gamma(\Phi''_{\rm con}\,\Phi''_{\rm el})] \supset \Gamma(\mu_a), \tag{4}$$

where μ_a is a molecule fixed component of the dipole moment. This μ_a can be expanded in the vibrational normal coordinates. For allowed electronic transitions, the first term in this expansion is the leading term. The contortional wave functions can be symmetric (s) or antisymmetric (a) with respect to reflection in a plane through the short molecular axis of T so they can be of a_1 or b_2 symmetry. For the selection rules of the contortional transitions follows $s \leftrightarrow s$, $a \leftrightarrow a$, $s \not\leftrightarrow a$. So if the approximations made are valid, we may expect a spectrum with two rotational bands. The distance between these bands is determined by the difference between contortional splittings in the ground and excited vibronic levels.

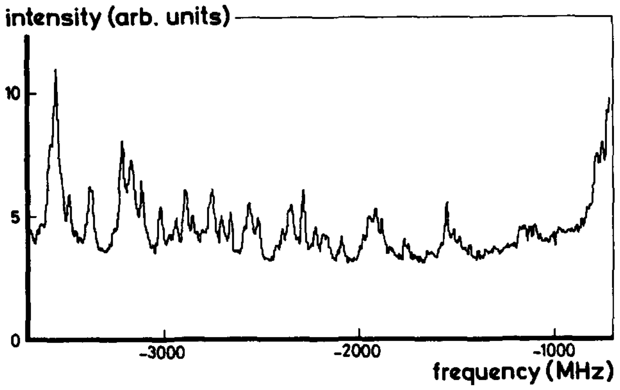

FIG. 6. Part of the P branch of the 471 cm^{-1} parallel band of the tetracene–argon vdW complex. The onset of the Q branch is at the right hand side of the figure.

C. The T–Ar vdW complex

The 0–0 and 311 cm^{-1} vibronic transitions in T both involve an a_g-type totally symmetric vibration in the S_1 electronic state. For the T parent molecule, the rotational bands proved to be identical. In the T–Ar vdW complex, again both states behave in the same way. The rotation-free transition frequencies are almost equally shifted (Table I) and the rotational band contours are nearly the same. This strongly suports the identification of the bands. The spectra show a characteristic perpendicular shape with pronounced Q branches (Fig. 5). It should be noted that this structure seems to be on a broad background. Such background was also found in the T molecule (Sec. III), but it looks larger in the T–Ar complex. Comparing the details of both transitions, it appears that small differences do exist. Because of the high density of states no single spectral lines are observed and it is difficult to estimate the exact linewidth. We assume that it is still Doppler limited. The 471 cm^{-1} nontotally symmetric b_{3g} vibrational mode of T gave rise to a weak parallel band. The corresponding transition in the T–Ar complex (Fig. 6) is shifted $-41.52(5)$ cm^{-1} but still has a clear parallel (a-type) shape. As the transition dipole moment conserves its orientation with respect to the parent molecule, we may conclude that the orientation of the a axis in the parent molecule and the complex is very much alike. This is in agreement with rotational constants derived from the model calculations. The observed spectral linewidth in the band is 15 MHz and thus still due to the experimental limitations. The expected natural linewidth on basis of lifetime measurements[11] is about 8 MHz.

All these rotational bands were single vibronic transitions. We did not find any evidence for a splitting of the vibrational states due to a potential barrier for movements along the long molecular axis. It is thus concluded that such barriers must either be small or the splittings in ground and excited vibronic states must be almost identical. It seems very unlikely that these equal splitting are the case for all three vibrational modes that have been studied.

Unfortunately, we did not succeed in assigning the rotational spectra of the T–Ar vdW complex. As this molecule has very small rotational constants, the spectra are extremely dense, even at a 15 MHz linewidth and a rotational tem-

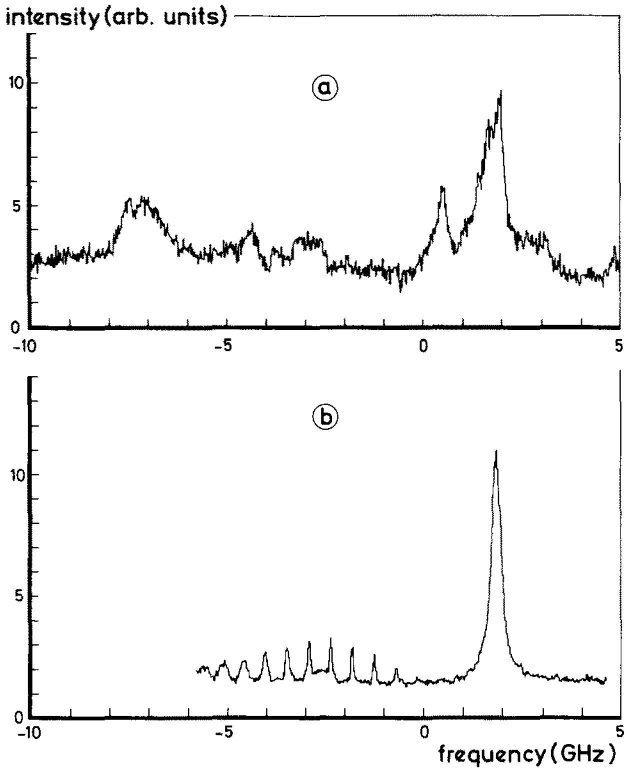

FIG. 7. Comparison between the 0–0 (b) and 311 cm^{-1} (a) rovibronic bands of the tetracene–krypton vdW complex.

perature of less than 3 K. Only in the case of the parallel band a limited number of single rotational lines was observed (Fig. 6). On the basis of the experimental resolution it should be possible to resolve and assign the rotational bands of a molecule as large as the T–Ar complex. Despite much effort, such an assignment could not be found. For example, the clear sequence of Q branches in the perpendicular bands looks distorted. In the parallel band there seems to be an excess of lines which is most clearly demonstrated by a rather broad Q branch. Although there is no incontestable proof, we are convinced that this appearance of extra lines is due to perturbations in the rotational spectra for the following reasons. It is very unlikely that the unexpectedly high spectral density is caused by a large asymmetry of the complex. On basis of the calculated geometry we expect an asymmetry parameter $\kappa = -0.97$. This is comparable with the value for the parent molecule ($\kappa = -0.966$). Both molecules are thus near prolate rotors. Geometrical changes in the complex structure hardly affect the asymmetry. We consider the calculated potential surface to be sufficiently reliable to rule out large deviations from the determined geometry. A change of geometry upon excitation might complicate the assignment of the spectrum. However, since the number of rotational states does not change, the number of rotational transitions should not be affected. A clear indication for the existence of a surplus of transitions in the T–Ar bands is given by the spectra of the T–Kr and T–Xe complexes were the effects are much more evident.

The parallel band (Fig. 6) of the T–Ar complex shows a structureless background signal. This background level is significantly stronger than observed in the parent molecule. For the perpendicular bands, the spectra are too dense to draw an unambiguous conclusion. From comparison of both spectra (Fig. 5) it is clear that there exists a difference in background level and that it is much higher for the 311 cm^{-1} band. The isotope effect of the carbon atoms, mentioned in Sec. III, is too small to account for the entire level in the 311 and 471 cm^{-1} bands. Another contribution may arise from a weak combination band. The transition dipole moment for the parallel band in the parent molecule is along the a axis, which is slightly rotated in the complex. Consequently the dipole moment has a component perpendicular to the a axis, which allows a weak perpendicular band. The transition dipole moment for the 311 cm^{-1} band, however, is along the b axis. The orientation of this axis in the complex is the same as in the parent molecule and so this will not give rise to hybrid bands. However, a substantial background is observed. It is felt that only the combination of transitions in isotopic species and combination bands cannot fully account for the observed backgrounds. The remaining part must be ascribed to a strong S_1-background state interaction. The nature of this effect has been discussed for T in Sec. III. Due to the increase in interstate coupling in the complex, as concluded from the spectroscopy, an increase in background signal might also be expected. As a speculative suggestion, we would also like to mention two other possible sources of the broad structureless background; (i) hot bands in the spectra of the complexes and/or (ii) effects of predissociation. There are, however, no clear indications in this direction and we will not further discuss them.

D. The T–Kr vdW complex

The observed red shift of the T–Kr vibronic transitions with respect to the T parent molecule is much larger than for the T–Ar complex as can be seen from Table I. The influence of the krypton atom on the vibrational levels in the ground and excited state of T is thus different from the influence of an argon atom. An indication of some large effects is also given by a shortening of the fluorescent lifetime of the complex to 7 ns[11], and a reduction of the excitation intensity. The rotational spectra of the T–Kr complex also clearly display the existence of strong perturbations in the excited electronic state.

The 0–0 transition and the transition related to the 311 cm^{-1} vibration in T have hardly any resemblance, as may be seen from Fig. 7. The 0–0 spectrum extends over a broad region of more than 100 GHz and suggests the presence of two transitions. There is a pronounced Q-like branch, typical for a parallel band, and at a distance of about 4 GHz, a number of smaller Q branches, characteristic for a perpendicular transition. Individual spectral lines are no longer observed. The 311 cm^{-1} vibronic transition shows an unrecognizable structure of some broad shallow patterns. The 471 cm^{-1} vibration involves a symmetry-forbidden transition in T. In the T–Kr complex, the excitation intensity is further decreased and the spectrum becomes very weak. It consists of a small hump on a broad background, without any further structure.

In none of the studied transitions in T–Kr we observed individual spectral lines. The expected linewidth on basis of the measured lifetime is about 25 MHz and exceeds the residual Doppler width. Therefore the line profile will become almost Lorentzian with tails which extend some way from the region of the peak. Combined with the high density of states, this causes spectral overlap.

The krypton atom in its natural occurrence is mainly found in four isotopes, with a relative abundance of about 12%, 12%, 57%, and 17% for ^{82}Kr, ^{83}Kr, ^{84}Kr, and ^{86}Kr, respectively. Of course this slightly affects the rotational spectra and gives rise to a smeared-out structure. The observed large effects though of the T–Kr spectra will be affected, but certainly not caused by the existence of the various isotopes.

Assuming the 0–0 vibronic transition consists of two rotational bands, the question arises if this could be caused by a contortional motion. However, this is very unlikely for the following three reasons. First, the model calculations show that the potential barrier for krypton should be smaller than for argon, and no effects were found for the T–Ar complex. Second, if coupling to the vibration is neglected, the rotational transitions to both contortional states should exist of the same type i.e., both spectra should be either parallel or perpendicular bands. Third, no evidence was found for a similar splitting in the 311, and 471 cm^{-1} T–Kr spectra, which involve low vibrational modes of the T parent molecule. On basis of model calculations mentioned before, we may rule out the existence of chemical isomers. Also, the possibility of a vdW vibrational mode causing an additional band, is rejected. The splitting between the two bands is too small for such a vibrational energy.

It is remarkable that, in spite of the differences in degree of perturbations in the rotational spectra, the redshift with respect to the T parent molecule is almost equal (Table I) for the different vibronic transitions. The relative increase in constant background in the T–Kr spectra should be noted. The increasing perturbation with excited state energy and the large linewidth point in the direction of a coupling of the S_1 electronic state with one or more other states.

E. The T–Xe vdW complex

The 0–0 rovibronic band of the T–Xe complex experiences the largest red shift [110.0(1) cm^{-1}] of all studied T–R molecules. It shows even less structure than the T–Kr spectra. Now there also exists a broad (> 100 GHz) background with only some small humps as structure in a 30 GHz region. No traces of individual lines have been observed, so the natural linewidth in the spectrum must be of considerable size. The decay lifetime has been estimated[11] to be 1.5 ns, corresponding to a linewidth of 100 MHz. It should be noted also that the abundant quantity of isotopic species present in a natural amount of xenon will obscure the spectrum.

The 0–0 band is quite weak, suggesting that the decay of the exited state is mainly of nonradiative character. We did not study other, even weaker, T–Xe rovibronic bands. The observed spectrum supports our conclusion about the existence of a coupling between the S_1 electronic state and dark background states in the complex. It is clear that this interaction is enhanced for heavier rare gases.

F. T–R_2 vdW complexes

As can be seen from Table I, a number of transitions of the T–R_2(R = Ar, Kr) vdW complexes have been studied. The shift of these rotational bands with respect to the corresponding transition in the host molecule is close but not equal to twice the shift of a T–R complex. From this the conclusion, it may be drawn that the second R atom occupies a position on the surface of the host molecule, which is geometrically inequivalent with the position of the first atom. From model calculations,[10] it is found that in the most favorable case, both R atoms are on the same side of the T molecular plane. The benefit of this geometry arises from the R–R interaction.

All transitions in the T–R_2 complex, mentioned in Table I, qualitatively behave in the same way. They show no individual lines, due to a large linewidth.[11] The spectra have hardly any structure and merely consist of a broad flat band. There are no indications that the spectra consist of a multiple of bands, due to, for example, chemical isomers.

V. CONCLUSION

It was shown that rotationally resolved spectra can be obtained from large organic molecules like tetracene and even its vdW complexes. We considerably improved the accuracy of several vibronic transitions in the host molecule as well as the T–R_n complexes. Rotational spectra of T have been assigned and molecular constants of the free molecule were obtained. The rigid planar structure of the parent molecule was deduced. It was also shown that there are no clear perturbations in the rotational spectra of the lower vibrational modes in the S_1 electronic state.

The spectral data of the T–R_n ($n = 1,2$) complexes confirm lifetime measurements. No clear effects of tunneling splittings were observed. Perturbations in the excited electronic singlet state are demonstrated. These effects are very small in the T–Ar molecule, more pronounced in T–Kr, and very large in T–Xe and T–R_2 complexes. It was observed that these perturbations increase with excited state energy, with the size of the complex, and with the mass of the inert gas atoms. It may then be connected to e.g., the different polarizabilities of these atoms. The spectral perturbations may be induced by S–T intersystem crossings, S_1–S_0 state mixing, or even by a coupling of the S_1 state with higher energy levels. The presence of such interaction is clearly demonstrated by the 471 cm^{-1} a-type transition. This band is symmetry forbidden but becomes allowed by coupling with the S_2 ($^1B_{1u}$) state. As the anomalous effects occur for different vibrational levels, Fermi resonances will not be its cause. Testing of available model calculations on the complex structure was not possible due to a lack of complete assignment of the rotational bands. However, the existence of chemical isomers for these small complexes is shown to be very unlikely.

A significant background level in the spectra of T as well as T–R_n molecules was observed. Part of this background can be attributed to isotopic species and hybrid bands. However, it is felt that there is strong evidence to ascribe a certain fraction of the background signals in the spectra to the above discussed interaction between the S_1 and other states.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. A. Majewski for suggesting the subject of this paper. We would like to thank the referee for his constructive remarks and suggestions. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek (FOM) and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO).

[1] E. Riedle, H. J. Neusser, and E. W. Schlag, J. Chem. Phys. **75**, 4231 (1981).

[2] S. M. Beck, M. G. Liverman, D. L. Monts and R. E. Smalley, J. Chem. Phys. **70**, 232 (1979).

[3] B. W. Keelan and A. Zewail, J. Chem. Phys. **82**, 3011 (1985).

[4] A. Amirav, U. Even, and J. Jortner, J. Chem, Phys. **75**, 3770 (1981).

[5] A. Amirav, U. Even, and J. Jortner, Chem. Phys. Lett. **72**, 21 (1980).

[6] W. Majewski and W. L. Meerts, J. Mol. Spectrosc. **104**, 271 (1981).

[7] W. L. Meerts, W. A. Majewski and W. M. van Herpen, Can. J. Phys. **62**, 1293 (1984).

[8] B. J. van der Meer, H. T. Jonkman, J. Kommandeur, W. L. Meerts, and W. A. Majewski, Chem. Phys. Lett. **92**, 565 (1982).

[9] W. M. van Herpen, W. L. Meerts, and A. Dymanus, Laser Chem. **6**, 37 (1986).

[10] M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, J. Am. Chem. Soc. **103**, 6586 (1981).

[11] A. Amirav, U. Even, and J. Jortner, J. Chem. Phys. **75**, 2489 (1981).

[12] J. P. Bekooy, W. L. Meerts, and A. Dymanus, J. Mol. Spectrosc. **102**, 320 (1983).

[13] U. Even, A. Amirav, S. Leutwyler, M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, Faraday Discuss. Chem. Soc. **73**, 153 (1982).

[14] I. Raitt, A. M. Griffiths, and P. A. Freedman, Chem. Phys. Lett. **80**, 225 (1981).

[15] A. Amirav and J. Jortner, Chem. Phys. **85**, 19 (1984).

[16] J. K. G. Watson, J. Chem. Phys. **46**, 1935 (1967).

[17] J. K. G. Watson, J. Chem. Phys. **48**, 4517 (1968).

[18] T. Torring, J. P. Bekooy, W. L. Meerts, J. Hoeft, E. Tieman, and A. Dymanus, J. Chem. Phys. **73**, 4875 (1980).

[19] J. Monteath Robertson, V. C. Sinclair, and J. Trotter, Acta Crystallogr. **14**, 697 (1961).

[20] R. B. Campbell and J. M. Robertson, Acta Crystallogr. **15**, 289 (1962).

[21] E. Riedle, H. J. Neusser, and E. W. Schlag, J. Phys. Chem. **86**, 4847 (1982).

[22] W. L. Meerts and W. A. Majewski, Laser Chem. **5**, 339 (1986).

[23] H. Saigusa and E. Lim, J. Chem. Phys. **78**, 91 (1983).

[24] S. Leutwyler and A. Schmelzer, J. Chem. Phys. **79**, 4385 (1983).

[25] P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic, New York, 1979), pp. 344–351.