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ROTATIONALLY RESOLVED SPECTROSCOPY OF DEUTERATED FLUORENE AND THE FLUORENE–ARGON VAN DER WAALS COMPLEX

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With a single frequency tunable UV source in combination with a collimated molecular beam, rovibronic fluorescence spectra were obtained for fully deuterated fluorene and its van der Waals complex with argon. The 0_0^0 vibronic band in both molecules was assigned and molecular constants derived. The argon atom in the complex lies above the middle ring of the fluorene molecule. It is shown that substantial zero-point motions are present in the complex, hindering a precise determination of the effective structure.

1. Introduction

In recent years several spectroscopic studies have been reported on large aromatic molecules and their van der Waals (vdW) complexes. In order to limit the population of numerous energy levels at room temperature in these large molecules, most work has been performed using molecular jet techniques. The reduction in the internal degrees of freedom in the expansion facilitates the interpretation of the otherwise congested spectra. The spectral resolution is generally sufficient to observe rovibronic bands in relatively small molecules such as the benzene–helium complex [1]. For larger molecules like fluorene (FL) only vibronic resolution is achieved in a jet. The electronic shift of some bands of FL–argon vdW complexes has been reported as well as the lifetime of the first electronic excited singlet S_1 state [2]. This shift is caused by the difference in interaction between FL and argon in the ground and excited state of the complex. The assignment of various vibronic bands of FL–R (R = Ne, Ar, Kr, Xe) complexes by a mass-resolved technique was reported by Leutwyler et al. [3].

To obtain information regarding the structure of the molecule or its complexes, rotational resolution is needed. Previous work showed that this can be achieved by using a strongly collimated molecular beam in combination with a narrow band radiation source [4]. The position of the out-of-plane hydrogen atoms in the FL molecule was determined from the rotational constants. The effective structure of the FL–Ar complex was also obtained. Yet such conclusions rest on some basic assumptions.

First, the frame of the parent molecule is considered to be a rigid rotor. The rotational constants however reflect the effective structure of the molecule, which may be different. For the determination of the position of the out-of-plane hydrogen atoms the "inertia defect" of the molecule is used [4]. This defect is affected by zero-point vibrations. These contributions were neglected in previous work. A check on the validity of this approximation can be made by comparing different isotopic species of the molecule. If the rigid-rotor approach is applicable, data from various isotopic species should yield the same effective structure.

A second problem concerns the derivation of the effective structure of the complex. Diagonalization of the inertia tensor results in a quadratic function in the coordinates of the argon atom in the centre of mass frame of FL. It is therefore not possible to distinguish between positive and negative signs of these coordinates. On isotope substitution the centre of mass of FL is shifted and the problem is transformed to a different axis system. In combining data from different isotopic species it is, therefore, in principle possible to derive a unique solution for the effective structure.

A third problem originates from the interpretation of the effective structure as derived from the rovibronic spectra. Recent theoretical work of Brocks et al. [5] has shown that the argon atom experiences a large-amplitude motion in the complex. This molecule cannot be considered to be a rigid rotor. An experimental indication that such motions are present may be found in spectroscopic work on different isotopes. A rigid-rotor molecule will yield the same effective structure for all isotopes. In a more floppy molecule the isotopomers may exhibit differences.

With these problems in mind we have measured the rovibronic 0_0^0 band of the fully deuterated fluorene molecule FL-d_{10} and its vdW complex with argon. A comparison is made with data from FL-h_{10} as reported in a previous paper [4].

2. Experimental

The measurements were performed using laser-induced fluorescence detection in a seeded molecular beam. The experimental apparatus has been described elsewhere [6]. FL-d_{10} with a 98.9% deuterium abundance (MSD Isotopes) was heated in a quartz source to about 110°C. With argon as seeding gas, a jet expansion was made from a 125 µm diameter nozzle. The typical backing pressure was 0.5 bar. Two diaphragms in a differential pumping system strongly collimated the molecular beam, which resulted in a residual Doppler linewidth of about 15 MHz. The molecular beam is crossed by a laser beam at a distance of 30 cm from the beam orifice. The total, undispersed fluorescence is collected and imaged to a photomultiplier tube. Data recording is performed by a standard photon counting system, interfaced with a microcomputer. The narrow band laser radiation is generated by intracavity frequency doubling of a cw single mode ring dye laser [7]. The 0_0^0 transition of FL-d_{10} around 294.9 nm is at the edge of the tuning range of the $LiIO_3$ doubling crystal, but still a typical UV power of 0.2 mW was obtained. This proved sufficient to record the spectrum at a 0.1 s time constant. Relative frequency calibration was carried out using a sealed temperature stabilized Fabry–Perot interferometer, while absolute frequency measurements were performed using an iodine reference absorption spectrum [8].

3. Results and discussion

3.1. Fluorene

The FL molecule can be characterized in C_{2v} symmetry. The molecule has a planar structure, apart from two out-of-plane hydrogen atoms protruding from the five membered ring. It is a near prolate asymmetric rotor with an asymmetry parameter $\kappa = -0.857$. The (a,b,c) principal axes are identified as (y,x,z) in fig. 1. The 0_0^0 band of FL-h_{10} has been studied previously [2–4]. It was shown to be a $S_1(^1B_2) \leftarrow S_0(^1A_1)$ singlet–singlet transition with a parallel-type rotational structure. The electronic transition dipole moment is along the a-axis in agreement with earlier conclusions from crystal spectra [9]. We measured the 0_0^0 band of deuterated FL-d_{10} under rotational resolution. The spectrum and its Q branch are well resolved. The observed linewidth is 15 MHz and is determined by the experimental limitations. We therefore conclude that the natural linewidth is smaller than 15 MHz and thus the lifetime of the FL-d_{10} excited S_1 state has a lower limit of 10 ns. The lifetime of the FL-h_{10} species has been reported as 23 ns [2]. The observed band was identified as an a-type rotational band. A total of 450 lines were assigned in a 30 GHz region, with the se-

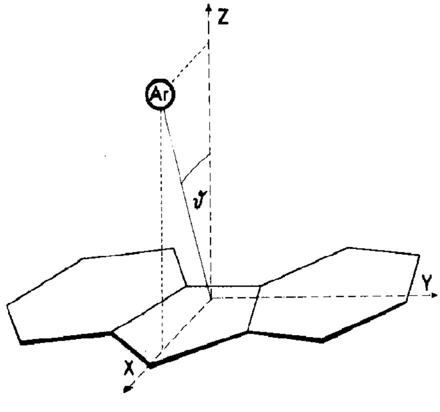

Fig. 1. Orientation of the coordinate system used for fluorene and the fluorene–argon complex. The origin is taken at the centre of mass of fluorene.

Table 1
Molecular constants (MHz) for the fluorene and fluorene-argon molecules in their S_0 and S_1 electronic states ($\Delta A = A' - A''$, etc.)

		FL-d_{10}	FL-d_{10}Ar
S_0	A''	1826.2(25)	754.4(38)
	B''	531.694(73)	416.74(13)
	C''	414.064(70)	370.54(13)
S_1	ΔA	−57.300(11)	−1.743(20)
	ΔB	5.735(13)	1.417(26)
	ΔC	0.459(12)	4.246(27)

lection rules for (K_{-1},K_{+1}): $(ee)\leftrightarrow(eo)$ and $(oe)\leftrightarrow(oo)$ where e means even and o odd. Lines with J up to 20 were fitted to an asymmetric rotor model [10] and gave an excellent fit with a standard deviation of 3.4 MHz. From the fit we obtained the rotational constants listed in table 1 and the rotationless transition frequency ν_0, given in table 2. The shift of ν_0 with respect to the FL-h_{10} species is 129.128(3) cm^{-1}.

The observed band contains a number of isolated single rotational lines. From the observed intensities we determined the rotational temperature T_{rot} in the molecular beam. The intensity of a transition is given by

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

Here $A(J'',K''_{-1},K''_{+1})$ can be approximated by the Hönl–London factors for a symmetric top molecule. The various pairs of equivalent nuclear spins in FL-d_{10} give rise to different spin statistical weights g_n. The values for g_n are: 29646 when (K_{-1},K_{+1}) is (ee) or (oo) and 29403 when (K_{-1},K_{+1}) is (eo) or (oe). These small differences in intensity are negligible in comparison with our experimental accuracy of about 5%. A fit of 100 line intensities to eq. (1) yielded a rotational temperature of $T_{rot} = 3.7(4)$ K. This temperature is somewhat higher than obtained in previous experiments because we used a rather low argon pressure to manage our supply of deuterated fluorene economically.

Table 2
Rotationless $S_1 \leftrightarrow S_0$ 0^0_0 transition frequencies (cm^{-1}) for fluorene [4] and the relative frequency shift $\Delta\nu = \nu - \nu_0(FL)$ of deuterated fluorene and the vdW complexes with argon

	ν_0	$\Delta\nu$
FL-h_{10}	33775.547(12)	
FL-h_{10}Ar		−43.952(3)
FL-d_{10} [a]	33904.675(12)	
FL-d_{10}Ar		−44.504(3)

[a] The absolute isotope shift can be determined more accurately: $\nu_0(\text{FL-}d_{10}) - \nu_0(\text{FL-}h_{10}) = 129.128(3)\ cm^{-1}$.

By simulation of the spectrum, using the obtained molecular constants and the derived rotational temperature, it appeared that all spectral features, even the weak ones, could be reproduced. There is no indication of any perturbations in the spectrum due to, for example, intersystem crossings or internal conversion [11,12].

As shown in ref. [4] it is possible to obtain information on the effective structure of the FL molecule. The carbon skeleton of the molecule is planar, as derived from crystalline data [13]. If it is assumed that the hydrogen atoms connected to the two six-membered rings are located in the same plane, there are only two out-of-plane atoms. Both hydrogens protruding from the five-membered ring are located in the xz plane, symmetrically around the xy plane. The moments of inertia along the principal axis $I_g (g = x, y, z)$ can be separated into contributions from the in-plane atoms I^0_g and a part arising from the out-of-plane atoms ΔI_g,

$$I_g = I^0_g + \Delta I_g \,. \qquad (2)$$

By defining the quantity Δ in an analogous way to the inertia defect of a planar molecule as

$$\Delta = I_z - I_x - I_y \qquad (3)$$

it can be shown that

$$\Delta = \delta - 2\sum_i m_i z_i^2 \,, \qquad (4)$$

with

$$\delta = I^0_z - I^0_x - I^0_y \,. \qquad (5)$$

In eq. (4) i indicates the out-of-plane atoms with mass m_i and position z_i. For FL this equation reduces to

$$\Delta = \delta - 4m_H z_H^2 \,, \qquad (6)$$

where $|z_H|$ is the effective distance to the xy plane. The hydrogen mass m_H has to be replaced by the mass m_D of the deuterium atom for the deuterated fluorene. The planarity condition for I_g^0 imposes $\delta=0$ if the zero-point motions are neglected. In that case we would expect that $\Delta(\text{FL-}d_{10}) \approx 2\Delta(\text{FL-}h_{10})$. For FL-$h_{10}$ $\Delta=-2.18(40)$ amu Å^2. From table 1 it can easily be shown that $\Delta=-6.71(45)$ amu Å^2 for the FL-d_{10} molecule. Thus there is apparently not a simple factor of two difference in the value of Δ for both fluorene isotopes. To account for the deviation a contribution from zero-point motions is necessary. If the standard values $r(\text{C-H})=1.09$ Å and $\angle(\text{HCH})=109.5°$ are assumed for the CH_2 group in fluorene one finds, by using eq. (6), $\delta=1.01(40)$ amu Å^2 and $\delta=-0.33(45)$ amu Å^2 for FL-h_{10} and FL-d_{10} respectively. These seem reasonable values. For comparison the inertia defect in the naphthalene molecule amounts $\delta=-1.4$ amu Å^2 and $\delta=-0.2$ amu Å^2 for fully deuterated naphthalene [6].

We conclude from the observed values of Δ for FL-h_{10} and FL-d_{10} that zero-point contributions cannot be entirely neglected in eq. (6). The derivation of an effective coordinate z_H for the out-of-plane hydrogen atoms therefore suffers from a substantial inaccuracy, due to the deficiency of the rigid rotor model.

3.2. Fluorene–argon

The O_0^0 band in the FL–Ar vdW complex is red-shifted with respect to the corresponding band in the FL molecule. It also exhibits a parallel a-type structure. The Q branch is only partially resolved. Part of the FL-d_{10}Ar O_0^0 band is shown in fig. 2. A total of 216 lines in the spectrum were assigned and fitted to the asymmetric rotor Hamiltonian. From the fit we obtain the molecular constants shown in table 1 and the rotationless transition frequency ν_0 indicated in table 2. The fit yields a standard deviation in the lines of 4 MHz. The linewidth in the spectrum is again determined by the residual Doppler width and amounts to 15 MHz. Within the spectral accuracy there is no background signal in the spectrum as was observed in the case of the tetracene–argon vdW complex [12]. A number of single rotational lines were observed in the spectrum. From their relative intensities a rotational temperature T_{rot} was derived, using eq. (1). It appears that under the same expansion conditions, the rotational temperatures of FL and FL–Ar are equal. With the use of eq. (1) and the derived constants the spectrum was simulated, as shown in fig. 2. All observed spectral lines could be accounted for within the experimental accuracy. The frequency shift $\nu_0(\text{FL–Ar})-\nu_0(\text{FL})$ of the complex with respect to the parent molecule is $-44.504(3)$ cm^{-1}. This is comparable with the value for the FL-h_{10} species of $-43.952(3)$ cm^{-1}.

As was shown in ref. [4], it is possible to derive an effective structure for the vdW complex, assuming the FL parent molecule is rigid. The inertia tensor of the complex $(I^c_{\alpha\beta})$ can be expressed as a function of the moments of inertia along the principal axes (I_x, I_y, I_z) of the bare molecule and the position (x_0, y_0, z_0) of the argon atom in this axis system. By diagonalizing $(I^c_{\alpha\beta})$ one obtains the moments of inertia of the complex along its principal

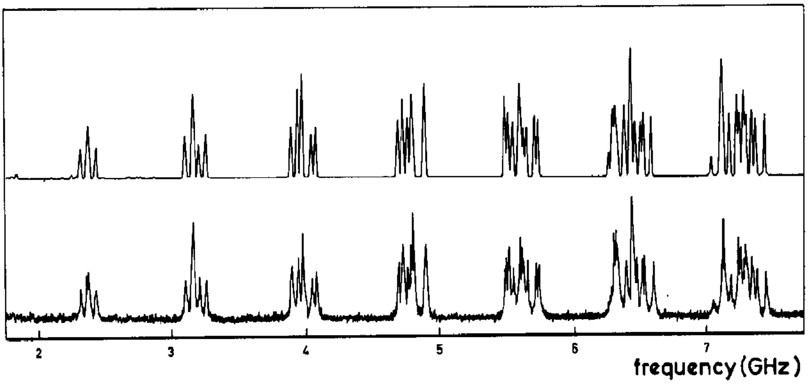

Fig. 2. Part of the R branch of the O_0^0 band of the deuterated fluorene–argon vdW complex. The calculated spectrum (top trace) is also shown. The indicated frequency scale is relative to the electronic origin of the band.

axis (ξ, η, ζ) as a function of (I_x, I_y, I_z). These moments are fitted to the experimental values. The value for y_0 is zero within the obtained accuracy. Obviously this could be expected because of the molecular symmetry plane. In the final fit we therefore kept the coordinate fixed at $y_0=0$. In that case the inertia tensor is simplified. By diagonalizing one obtains (I_ξ, I_η, I_ζ). It can be shown that if ΔI^c is defined as

$$\Delta I^c = I_\xi + I_\eta - I_\zeta - (I_x + I_z - I_y)\,, \qquad (7)$$

it follows that $\Delta I^c = 0$ only if both molecules are rigid rotors. With the molecular constants from table 1 we find $\Delta I^c = -12(5)$ amu Å^2 in the ground as well as in the excited state, thus deviating from zero. The difference can be accounted for by zero-point vibrations in both the parent molecule and the complex. These contributions cannot be entirely neglected, indicating that both molecules are not ideal rigid rotors.

By fixing the value of y_0 the degrees of freedom are reduced and only two moments of inertia of the complex are needed to solve for x_0 and z_0. Since ΔI^c in eq. (7) is not exactly zero, we obtain slightly different solutions, depending on which pairs of constants are used. This gives a good indication of the obtained accuracy. In the centre of mass frame of FL-d_{10} we find $|x_0| = 0.31(10)$ Å, $y_0=0$, $|z_0| = 3.46(3)$ Å, or by defining r_0 and θ as indicated in fig. 1: $r_0 = 3.46(3)$ Å, $|\theta| = 8.8(1.0)°$. The accuracy is not limited by the experimental uncertainty in the molecular constants but by the fact that the molecules do not behave as ideal rigid rotors.

The derived coordinates cannot be directly compared with those from FL-h_{10} as given in ref. [4]. One has to transform between the different centre of mass frames. This centre of mass can be calculated from the structure of the carbon skeleton [13] and the assumption that all CH bonds point along the line connecting the carbon atom and the centre of the six-membered ring. The bond length is taken as 1.08 Å. For the two out-of-plane hydrogens the bond angle with the molecular plane is taken as $\theta = 43°$. This structure reproduces the molecular constants for FL-d_{10} and FL-h_{10} within 0.6% and therefore seems reliable. The centres of mass are positioned on the intersecting line of the xz and xy plane. Their x coordinates differ by only 0.01 Å. In the centre of mass frame of FL-d_{10} the argon position as derived in ref. [4] would be $x_0 = 0.52(7)$ Å or $x_0 = -0.54(7)$ Å, $y_0 = 0$ and $|z_0| = 3.42(3)$ Å. We note that the agreement between the two possible structures is marginal and consequently a distinction between the two possible values of x_0 cannot be made. The uncertainty in x_0 exceeds the small displacement (0.01 Å) of the centre of mass by almost an order of magnitude. The small shift is caused by the fact that most deuterium atoms are positioned symmetrically around the centre of mass. A maximum shift would be reached by substituting only hydrogen and carbon atoms with positive x coordinates by their heavier isotopes. In this way a theoretical shift of the centre of mass of 0.06 Å may be expected. This is still rather small compared to the uncertainty in x_0.

We conclude that a distinction between two possible effective structures of the complex cannot be made. This is not caused by the fact that the accuracy in the obtained molecular constants is insufficient but by the fact that the parent molecule and its vdW complex are not ideal rigid rotor molecules. Contributions from zero-point vibrations are clearly present. The data confirm the proposal of Brocks et al. [5] that the argon atom in the complex experiences large amplitude motions (with amplitudes ≈ 0.3 Å).

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