

The structure of fluorene ($C_{13}H_{10}$) and the fluorene-argon van der Waals complex from a high-resolution near ultraviolet spectrum

W. LEO MEERTS, W. A. MAJEWSKI,¹ AND W. M. VAN HERPEN

Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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The high-resolution fluorescence excitation spectrum of the fluorene molecule and its van der Waals complex with argon has been studied. Rotationally resolved spectra were obtained by combining a well-collimated supersonic molecular beam with a single frequency tunable ultraviolet (uv) source. The $S_1 \leftarrow S_0 O_0^0$ vibronic transitions in fluorene and fluorene-argon were observed. The rotational constants of both molecules were determined and from these the structure of the fluorene-argon complex has been deduced. The argon atom is located above the middle five-membered ring. The coordinates of the position vector of the argon atom in the complex in the centre-of-mass system of fluorene are $r = (3.46 \pm 0.03) \text{ \AA}$ and $\vartheta = \pm (8.8 \pm 1.0)^\circ$. A model calculation of the fluorene-Ar structure was found to be in quite good agreement with the experimental result. The newly introduced inertial defect of the complex $\Delta I^c = -7(3) \text{ amu \AA}^2$ provided an experimental measure of the zero-point motion of argon in the complex.

On a étudié à haute résolution le spectre d'excitation de fluorescence de la molécule de fluorène et de son complexe de van der Waals avec l'argon. On a obtenu des spectres résolus rotationnellement en combinant un faisceau moléculaire supersonique à bonne collimation avec une source UV à fréquence unique ajustable. Les transitions vibroniques $S_1 \leftarrow S_0 O_0^0$ dans le fluorène et dans le complexe fluorène-argon ont été observées. On a déterminé les constantes rotationnelles des deux molécules et on en a déduit la structure du complexe fluorène-argon. L'atome d'argon est situé audessus de l'anneau central à cinq membres. Les coordonnées du vecteur position de l'atome d'argon du complexe, dans le système du centre de masse du fluorène, sont $r = (3,46 \pm 0,03) \text{ \AA}$ et $\vartheta = \pm (8,8 \pm 1,0)^\circ$. Un calcul de modèle de la structure fluorène-Ar a donné un très bon accord avec le résultat expérimental. Le défaut inertiel du complexe $\Delta I^c = -7(3) \text{ uma \AA}^2$ introduit récemment a fourni une mesure expérimentale du mouvement de point zéro de l'argon dans le complexe.

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1. Introduction

Laser spectroscopy in combination with molecular beams is a powerful tool in the investigation of the structure and dynamic behaviour of large molecules and their van der Waals complexes. In most experiments, the laser crosses the molecular beam close behind the nozzle. In this "free jet" setup, high sensitivity and moderate resolution are achieved. The line widths of the transitions are generally limited by the Doppler width, which is, in a free jet experiment, typically 600 MHz. This resolution is high enough for single vibronic excitation and shows the rotational structure in smaller organic molecules and their complexes, such as, for example, benzene-helium (1). For larger multi-ring compounds, higher resolution is required to observe more than the rotational contour. Rotational resolution not only facilitates structure determination of van der Waals complexes, but becomes a necessity for studies of larger molecules and complexes.

We achieved a considerable reduction of the Doppler width by increasing the distance between the source and the laser excitation region while strongly collimating

the molecular beam (2, 3). In this way, line widths as narrow as 15 MHz were observed. At such high resolution, not only could the rotational spectrum of naphthalene be studied (3), but also the molecular eigenstates in pyrazine (4) were revealed.

Single vibronic excitation spectra of the fluorene (F) molecule ($C_{13}H_{10}$) and its complexes with argon ($F-Ar_n$) were reported before in several papers (5, 6). In the present work, we studied the $S_1 \leftarrow S_0 O_0^0$ vibronic transition in F and F-Ar. We observed well-resolved rotational spectra in both molecules. From the rotational analysis it has been concluded that the skeleton of the bare fluorene molecule is planar, in accord with the crystalline work (7). The position of the out-of-plane hydrogens could also be determined. From the difference in the moments of inertia of fluorene and fluorene-argon, the structure of the complex has been deduced. The argon atom is located above the five-membered ring in the symmetry plane that bisects the molecule. An intensity analysis has been performed yielding the rotational temperatures of F and F-Ar in the molecular beam. Within experimental uncertainty, a Boltzmann distribution was found with equal temperatures for the bare molecule and the complex.

A calculation of the potential energy surface between the fluorene molecule and the argon atom using

¹Present address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6.

atom-atom interactions has been carried out. The result of this calculation is gratifying since it is in agreement with the experimentally determined structure of the complex.

In analogy with the inertial defect for a planar molecule (8), we have introduced the inertial defect for the complex (ΔI^c). If the argon atom in the complex is located in the bisecting plane, ΔI^c should be zero for the equilibrium structure. Deviations of ΔI^c from zero are a measure of the contributions due to the vibrational motion of the argon in the complex. Experimentally, a significant value for ΔI^c has been determined.

All observed lines in both F and F-Ar could be assigned as pure rovibronic transitions. No perturbations such as in pyrazine (4) or pyrimidine (9) were found in the excited singlet S_1 states of F and F-Ar, which demonstrates the absence of any significant inter-system crossings in fluorene.

2. Experimental

The experimental setup has been described in detail before (3); only the most relevant features will be discussed here. The seeded beam technique has been used to reduce the internal temperature of the molecules in the beam. This not only simplifies the rovibronic spectra considerably, but complexes are also readily formed in the ultracold beam. A mixture of 1% fluorene and argon was expanded through a 100- μm nozzle. The total backing pressure was 5 bar (1 bar = 100 kPa) and the reservoir was heated to 190°C. In order to achieve rotational resolution, the molecular beam was strongly collimated by two diaphragms with a two-step differential pumping system. The interaction zone, where the laser beam crossed the molecular beam, was 30 cm from the source. This setup reduced the Doppler width to 15 MHz. Fluorescence excitation spectra were obtained by collecting the undispersed total fluorescence. The image of the fluorescing spot was focused on the photocathode of an EMI 9864/950 QA photomultiplier and measured by a standard photon counting system.

The narrow band ultraviolet (uv) radiation has been obtained by our recently developed method of second-harmonic generation (SHG) (10). The SHG is achieved by placing a LiIO_3 angle-tuned crystal in a modified Spectra Physics ring dye laser. Stabilized scans over 4 cm^{-1} with a line width of less than 0.5 MHz could easily be made. About 1 mW of continuous wave (cw) power has been applied at the interaction zone. The absolute frequency calibration has been performed on the fundamental frequency by a 1-m monochromator and the calibration absorption spectrum of iodine (11). The relative frequency has been measured by a sealed off, temperature stabilized confocal Fabry-Perot interferometer with a 299.32-MHz free spectral range.

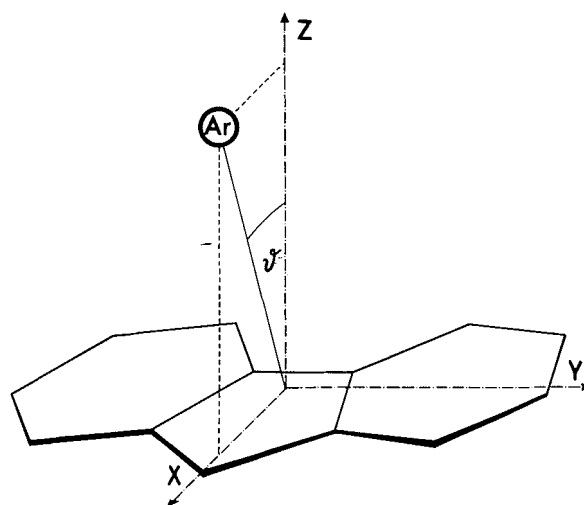


FIG. 1. Definition of the coordinate system as used for fluorene and the fluorene-argon complex. The origin of the coordinate system has been chosen at the centre of mass of the fluorene.

3. Results and discussion

3.1 Fluorene

The low-resolution single vibronic spectrum has been studied before (5, 6). The strong transition at 296 nm has been assigned as the O_0^0 band of the $S_1(^1B_2) \leftarrow S_0(^1A_1)$ electronic transition. We have investigated this transition under high resolution. A completely rotationally resolved spectrum was obtained consisting of several hundreds of lines in a 100-GHz region. Even most of the Q -branch transitions were resolved. The typical count rate for a single line was 35 000 counts/s. On basis of its structure (7), fluorene can be characterized as a near prolate asymmetric rotor with the a axis along the long axis (y axis in Fig. 1). The rotational spectrum we observed was uniquely identified as an a -type transition. The electronic transition is, therefore, long-axis polarized, in agreement with the conclusion from the crystal spectra (12). A region of 20 GHz around the pure vibronic transition frequency ν_0 was investigated in detail. A total of 225 rotational transitions were assigned in this region. All features, even the very weak ones with the rotational quantum number J as high as 19, were identified. The transitions were fit to an asymmetric rotor model yielding the assignments of the lines, the rotational constants in the ground and excited electronic state, and ν_0 . An excellent fit was obtained with a standard deviation of 7.5 MHz for the lines. The resulting molecular constants are given in Table 1.

Furthermore, it was carefully investigated whether any extra features due to intersystem crossings were observable. In contrast to the situation in pyrazine (4)

TABLE I. Molecular constants of fluorene and fluorene-argon in their S_0 and S_1 electronic states ($\Delta A = A' - A''$, $\Delta B = B' - B''$, $\Delta C = C' - C''$)

		Fluorene	Fluorene-argon
S_0	A'' (MHz)	2 183.2(33)	811.1(29)
	B'' (MHz)	586.520(69)	468.58(14)
	C'' (MHz)	463.239(65)	401.58(13)
S_1	ΔA (MHz)	-73.387(14)	-1.402(27)
	ΔB (MHz)	6.716(38)	1.437(31)
	ΔC (MHz)	0.734(41)	4.961(26)
	ν_0 (cm^{-1}) ^a	33 775.547(5)	33 731.595(5)

^aThe shift can be determined more accurately: $\nu_0(\text{F-Ar}) - \nu_0(\text{F}) = -43.952(3) \text{ cm}^{-1}$.

and pyrimidine (9),² the spectra of fluorene and also the F-Ar complex were pure unperturbed rotational spectra. Although it is expected that such a large molecule as fluorene would be in the range of the "statistical limit" (13), the present result indicates that the interaction between the S_1 and the background states is very weak. Furthermore, the lifetimes (23 ns) of the S_1 states (5) are so long that the natural line widths of these states (7 MHz) are still expected to be smaller than our Doppler limited line widths. This is in accord with the experimental observations.

The observation of single rotational transitions over a wide range of rotational states enabled us to determine the rotational (rot) temperature T_{rot} of the molecules in the beam. For a Boltzmann population distribution, the intensity of a single rovibronic transition is given by

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

where J'' , K''_{-1} , and K''_{+1} are the rotational quantum numbers of the ground electronic state with rotational energy $E(J'', K''_{-1}, K''_{+1})$ and I_0 is a constant. For a near prolate asymmetric top, $A_{J''K''_{-1}K''_{+1}}$ can be approximated by the Hönl-London factors for the prolate symmetric top limit (14). The coefficient g_n denotes the statistical weight due to the nuclear spins. The fluorene molecule can be characterized by the C_{2v} molecular symmetry group. The molecule has five pairs of equivalent hydrogens; four pairs in the plane of the skeleton and one pair out of this plane. The values for g_n are (e = even, o = odd)

$$g_n = 496 \text{ for } (K''_{-1}, K''_{+1}) = (\text{ee}) \text{ or } (\text{oo})$$

$$g_n = 528 \text{ for } (K''_{-1}, K''_{+1}) = (\text{eo}) \text{ or } (\text{oe})$$

These two numbers differ by only 6%. The observed intensities have typical uncertainties of up to 5–10%.

²As an example, this can easily be verified for the alkaliyanides using the results from ref. 17.

Therefore, the effects due to the nuclear spin statistics are negligible within experimental errors. The reason that the two values for g_n are so close is that a large number of hydrogens in fluorene are only pairwise at equivalent positions.

The relative intensities from the rotational spectrum were fitted to [1] with T_{rot} as the only parameter. A single rotational temperature could be assigned, $T_{\text{rot}} = 2.3(3) \text{ K}$.

Although a structure determination is impossible for fluorene with only the rotational constants from Table I, these data contain direct information about the position of the two out-of-plane hydrogens. It has been shown from crystalline work (7) that the carbon skeleton of the fluorene molecule is planar. Furthermore, it is obvious that the hydrogens on the six-membered rings are in the same plane. The two remaining hydrogens bound to the carbon in the bisecting plane are located in the xz plane symmetrically around the xy plane (see Fig. 1). Let us separate the contributions to the moments of inertia along the principal axes I_g ($g = x, y, z$) into a part containing the contributions from the atoms in the xy plane (I_g^0) and a part arising from the out-of-plane hydrogens (ΔI_g):

$$[2] \quad I_g = I_g^0 + \Delta I_g$$

Let

$$[3] \quad \Delta = I_z - I_x - I_y = (I_z^0 - I_x^0 - I_y^0) + (\Delta I_z - \Delta I_x - \Delta I_y)$$

Neglecting zero-point motions, the planarity conditions for I_g^0 impose

$$[4] \quad I_z^0 - I_x^0 - I_y^0 = 0$$

The accuracy of this equation is determined by the contributions to I_g^0 from the zero-point motions. We estimate that a value of $0.2 \text{ amu } \text{Å}^2$ is a good upper limit for these contributions. It can easily be seen that

$$[5] \quad \Delta = -2 \sum_i m_i z_i^2$$

where i represents the out-of-plane atoms with mass m_i and position z_i . For fluorene, the sum simply reduces to $-4m_{\text{H}}z_{\text{H}}^2$; $|z_{\text{H}}|$ is the distance to the xy plane. The values for I_g are readily obtained from the rotational constants given in Table 1 by using $I_a = h/8\pi^2A$, $I_b = h/8\pi^2B$, and $I_c = h/8\pi^2C$, and the correlation $(a, b, c) \rightarrow (y, x, z)$. Substitution yields $\Delta = -2.18(40) \text{ amu } \text{Å}^2$ and $|z_{\text{H}}| = 0.74(5) \text{ Å}$. By defining θ_{H} as the angle between the CH bond of the out-of-plane hydrogens and the xy plane, and r_{CH} as the length of this bond, it follows that $z_{\text{H}} = r_{\text{CH}} \sin \theta_{\text{H}}$. Within the present accuracy of z_{H} , the CH bond length may be assumed to be $r_{\text{CH}} = 1.08 \text{ Å}$, as in many methyl groups; therefore,

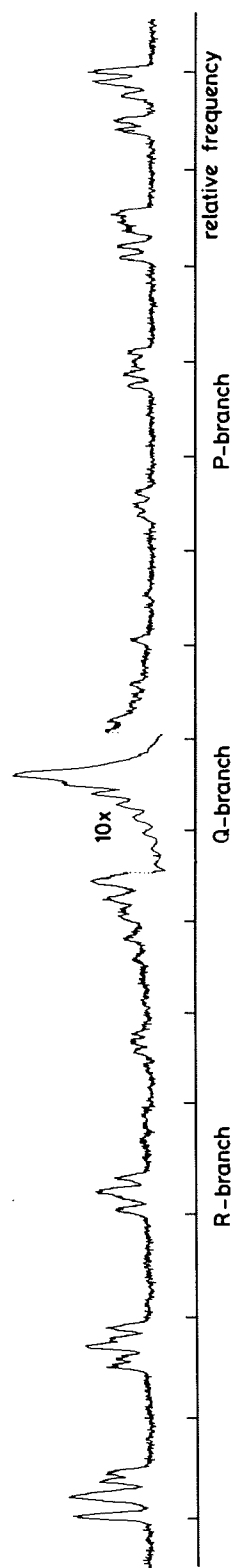


FIG. 2. Rotationally resolved spectrum of the fluorene-argon complex near the electronic origin of the O_0^0 transition at $33\,731.595\text{ cm}^{-1}$. The frequency markers are at every 598.64 MHz .

TABLE 2. Calculated and observed moments of inertia for fluorene (in units of amu \AA^2)

	Calculated value	Experimental value
$I_y(I_a)$	231.1	231.5(3)
$I_x(I_b)$	866.71	861.66(10)
$I_z(I_c)$	1095.63	1090.97(15)

$\theta_H = (43 \pm 4)^\circ$. This determines the position of the out-of-plane hydrogens.

The moments of inertia of the fluorene molecule can be calculated from the structure of the C skeleton (7) and the assumption that the CH distances from the in-plane hydrogens equal 1.08 \AA , while the CH bonds point along the line between the centre of the six-membered ring and the connecting carbon atom. The result of this calculation is given in Table 2. The calculated and experimental values agree to within 0.6%, which is very satisfactory. This demonstrates that the structures of the free fluorene molecule and the fluorene in the crystalline state do not differ significantly.

3.2 Fluorene-argon

Shifted about 44 cm^{-1} to the red side of the fluorene O_0^0 transition, a spectrum has been observed that was identified as that of the F-Ar complex. The transition was about a factor of 100 weaker than that of the bare fluorene molecule. The central 9-GHz part of the F-Ar spectrum is shown in Fig. 2. It shows a typical a -type spectrum with an unresolved Q-branch and well-resolved P- and R-branches. A total of 151 rotational transitions in a region of 23 GHz around ν_0 were identified and fitted to an asymmetric rotor Hamiltonian. Again an excellent fit was obtained, with a standard deviation for the lines of 7.6 MHz. The best fit rotational constants and ν_0 for F-Ar are presented in Table 1.

For the F-Ar complex, we were also able to derive a rotational temperature from the intensity measurements of the assigned rotational transitions. In the complex, the effects of the nuclear spin statistics on the intensities are even smaller than for fluorene itself, because of the lower symmetry of the complex (see below). Again a Boltzmann distribution was found with $T_{\text{rot}} = 2.1(4)\text{ K}$. The rotational temperature of the F-Ar complex in the beam is, to within the experimental accuracy, equal to that of the bare fluorene molecule. This result demonstrates that internal heating by complex formation is probably lost in the full expansion of the molecular beam.

We shall now show that the position of the argon in the complex can be determined from only the change in the moments of inertia from the bare molecule to the complex. This allows a structure determination of the

complex even without accurate knowledge of the structure of the bare molecule. In the following, we assume that in the complex the structure of the molecule is unaltered. We take I_x , I_y , and I_z as the moments of inertia of the bare molecule along its principal axes, x ,

y , and z respectively. In Fig. 1 these axes are indicated for fluorene. Let (x_0, y_0, z_0) be the position of the argon atom in the complex defined in the principal axis system of the molecule, then some simple mechanics yields the moment of inertia tensor of the complex ($I_{\alpha\beta}^c$):

$$[6] \quad (I_{\alpha\beta}^c) = \begin{bmatrix} I_x + \mu(y_0^2 + z_0^2) & -\mu x_0 y_0 & -\mu x_0 z_0 \\ -\mu x_0 y_0 & I_y + \mu(x_0^2 + z_0^2) & -\mu y_0 z_0 \\ -\mu y_0 z_0 & -\mu y_0 z_0 & I_z + \mu(x_0^2 + y_0^2) \end{bmatrix}$$

with μ the reduced mass $M_{Ar}M_F/(M_{Ar} + M_F)$. A diagonalization of ($I_{\alpha\beta}^c$) gives the moments of inertia of the complex ($I_{\xi}^c, I_{\eta}^c, I_{\zeta}^c$) along its principal axes (ξ, η, ζ) as a function of (x_0, y_0, z_0) . By fitting ($I_{\xi}^c, I_{\eta}^c, I_{\zeta}^c$) to the experimental values from Table 1, we determine $|x_0| = 0.53(7)$ Å, $y_0 = 0$, and $|z_0| = 3.42(3)$ Å. The argon atom is, therefore, located in the bisecting plane of the molecule at a distance from the centre of mass of fluorene of $r = (3.46 \pm 0.03)$ Å with $\vartheta = \pm(8.8 \pm 1.0)^\circ$ (see Fig. 1). To within these uncertainties, the structure in the ground and excited electronic states are found to be equal. The ambiguity in the sign of ϑ originates in the fact that the diagonalization of ($I_{\alpha\beta}^c$) yields a quadratic function in x_0, y_0 , and z_0 . Because of the symmetry of fluorene, it follows that the Ar atom in F-Ar is located above either the positive or negative x axis. Intuitively it might be expected that the argon atom is "pushed" towards the negative x direction by the steric effect of carbon and hydrogen atoms in the xz plane.

In an attempt to remove the ambiguity of the F-Ar structure, we carried out a model calculation of the potential surface of the F-Ar complex using the method described by Ondrechen *et al.* (15). The structure of fluorene discussed in Sect. 3.1 has been adopted. An absolute minimum in the energy was found for argon at the coordinates (in angstroms) $(x_0, y_0, z_0) = (0.13, 0, 3.48)$ with respect to the centre-of-mass coordinate system of fluorene (Fig. 1). Figure 3 shows three cuts through the coordinates of the potential minimum. The absolute potential minimum is above the central five-membered ring. In Fig. 3a we have indicated the two possible experimental positions. Because of the large anharmonicity of the potential surface in the x direction, the expectation value of the x coordinate in the ground vibrational state of the complex will be shifted considerably, with respect to the equilibrium distance, towards the negative x direction. The magnitude of this shift, although hard to estimate, can be as large as 0.5 Å. A molecular dynamics calculation such as discussed by Brocks *et al.* (16) is needed to get a

more accurate value for this shift. Work in this direction is in preparation; however, at the present stage we might conclude that the potential anharmonicity will favour the experimental structure labelled as 1 in Fig. 3a, i.e., a negative x value. The large maximum in the potential energy for positive x values is dominated by the contributions of the out-of-plane hydrogen. A better picture of the fluorene-argon potential along the x axis is obtained by plotting the minimum of the potential relaxing the z coordinate. The result of this calculation is depicted in Fig. 4. The effect of the out-of-plane hydrogens clearly shows up in the fact that the minimum in the potential energy is found for larger values of z near these hydrogens. The large maximum from Fig. 3a is now removed. However, the large anharmonicity in the x direction is still present, thus favouring structure 1 from Fig. 3a. A gratifying quantitative agreement is, therefore, obtained between the rather simplified model calculations and the experimental structure of the F-Ar complex.

The potential surface, especially in the y direction, is very flat. This will allow for large amplitude motions of the argon atom in the complex, which gives rise to large zero-point motion effects. In the case of F-Ar, an experimental measure can be obtained for these effects. In analogy with the inertial defect for a planar molecule (8), we shall call this the inertial defect of the complex (ΔI^c). For $y_0 = 0$ ($\eta \parallel y$) it can easily be shown from [6] that

$$[7] \quad \Delta I^c = [I_{\xi}^c + I_{\zeta}^c - I_{\eta}^c] - [I_x + I_z - I_y]$$

must be equal to zero if the zero-point motion contributions are neglected. With the results from Table 1, we find $\Delta I^c = -7(3)$ amu Å² for both the ground and the excited electronic states. The accuracy of the experimental structure is mainly limited by the value of ΔI^c . This also prevents observation, within the experimental accuracy, of a change in the structure of the complex upon electronic excitation. The inertial defect is not equal to zero, because only for the equilibrium

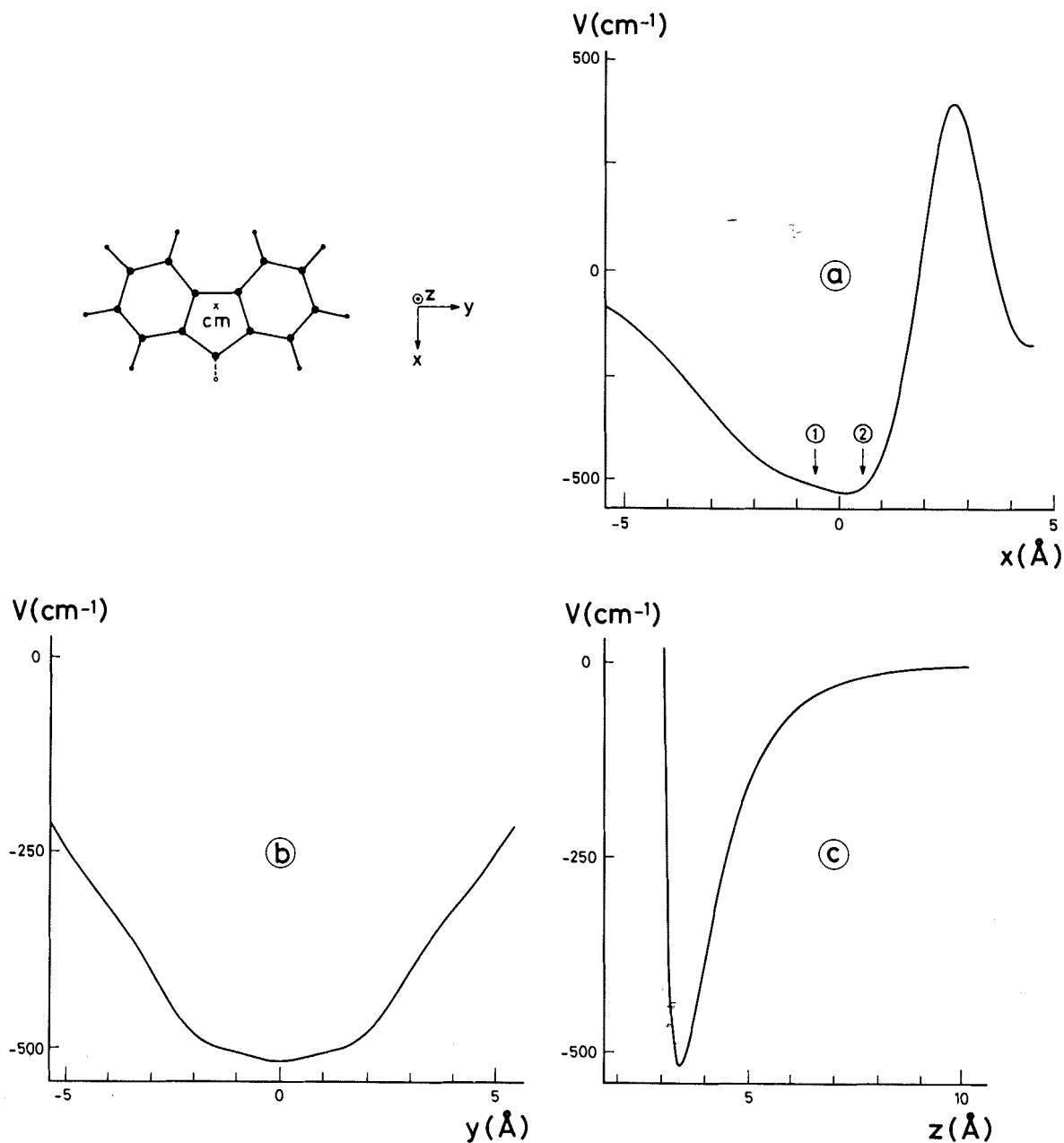


FIG. 3. Potential energy curves for a single argon with fluorene. The energy is drawn vs. the position (in angstroms) of the argon atom in the centre-of-mass coordinate system of fluorene (see insert). (a) Energy as a function of x along the line ($y = 0, z = 3.48$). The two arrows indicate the two possible experimental positions. (b) Energy as a function of y along the line ($x = 0.13, z = 3.48$). (c) Energy as a function of z along the line ($x = 0.13, y = 0$).

configuration does I_k exactly equal $h/8\pi^2 A_k$. In a given vibrational state, the vibrational averaging gives rise to deviations, since $\langle 1/r^2 \rangle \neq 1/\langle r^2 \rangle$. It is expected that similar to the inertial defect for a planar molecule,² a molecular dynamics calculation (16) of the complex will yield quite an accurate prediction for ΔI^c , which

directly measures the contributions to the vibrationally averaging process. This will provide an excellent test of the shape of the potential.

In conclusion, we have shown that rotationally resolved electronic spectra can be obtained for complexes with organic molecules even as large as fluorene. At

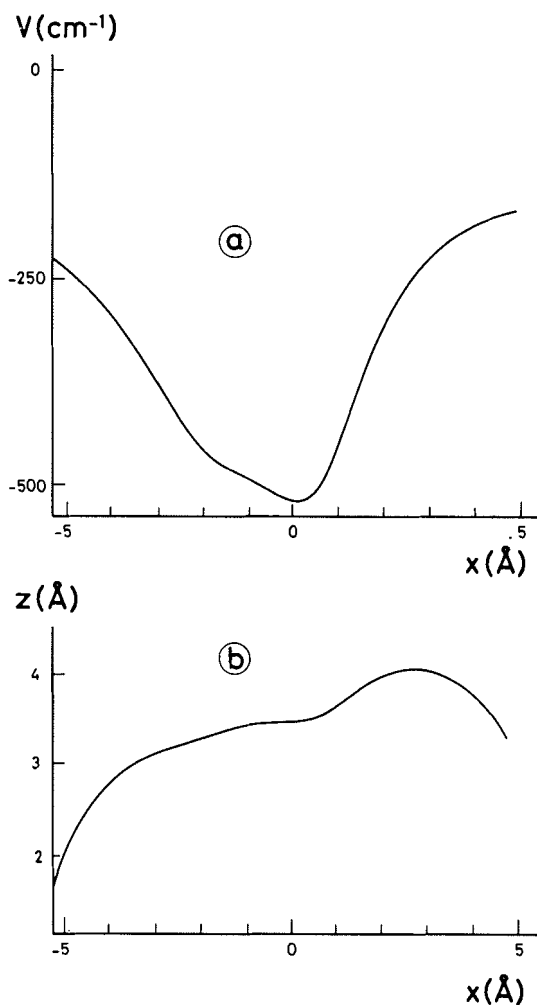


FIG. 4. The minimal potential interaction energy between fluorene and argon in the xz plane ($y = 0$). (a) Minimal potential energy vs. the x coordinate (z adjusted). (b) The z coordinate corresponding to minimum energy.

present there remains some ambiguity in the sign of the positional angle ϑ of the argon atom in the complex. This problem can be solved by studying the rovibronic spectrum of a deuterated fluorene - argon complex. Such an experiment is currently underway.

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