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Microsolvation of aromatic molecules by argon: Structure of fluorene-(Ar)₂ from high-resolution ultraviolet spectroscopy

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We present the high-resolution UV spectrum of the $0_0^0(S_1 \leftarrow S_0)$ transition in fluorene-(Ar)₂ recorded by mass-selective resonance-enhanced two-photon ionization with a pulsed narrow-band laser system ($\Delta\nu=140$ MHz). The measured *b*-type rotational structure of the strongest band at $33\,692.51\text{ cm}^{-1}$ in fluorene-(Ar)₂ allows the exclusion of a (2|0) structure for this band with the two Ar atoms placed on one side of the substrate. The observation of a *b*-type rotational transition is proof of a specific opposite sided (1|1) structure with the two Ar atoms placed above (and below) the central five-membered ring and one remaining sign ambiguity concerning the short in-plane axis coordinate. © 1994 American Institute of Physics.

I. INTRODUCTION

Fluorene has been used as a prototype molecule for the investigation of the solvation behavior of large aromatic systems in different solvents. Experimentally, microsolvation was realized in a supersonic beam with strong cooling. Vibronic spectra of the fluorene molecule (C₁₃H₁₀) and fluorene-(Ar)_{*n*} van der Waals complexes have been reported in several publications.¹⁻³ Considering the rigid planar fluorene molecule as a microsurface, the question arises whether two Ar atoms attach as an Ar dimer on one side [(2|0) structure], or on opposite sides [(1|1) structure].

Recently, we derived the structure of the carbazole-(Ar)₂ complex from Doppler free spectra obtained by mass-selective resonance-enhanced two-photon ionization. We clearly found the Ar atoms placed on opposite sides of the carbazole plane [i.e., a (1|1) structure], in line with the conclusions from rotational coherence spectroscopy in the time domain.⁴ This is remarkable because a (2|0) structure was concluded from low-resolution spectra assisted by molecular dynamics calculations.⁵ Here we would like to address the question whether fluorene-(Ar)₂ is an additional example for a (1|1) structure, which has been proved by rotationally resolved UV spectroscopy for *s*-tetrazine-(Ar)₂⁶ and benzene-(Ar)₂.^{7,8} A different solvation behavior may be expected for larger aromatic molecules with several energetically favorable positions of the noble gas atoms on the large substrate. Hitherto carbazole-(Ar)₂ is the only example for a three-ring aromatic substrate where a (1|1) structure has been identified by frequency domain spectroscopy.^{9,10} Fluorene is another interesting example because it has two hydrogen atoms which are located above and below the plane of the central five-membered ring. This might lead to preferred positions of the Ar atoms above the external benzene rings either on one or two sides of the molecular plane.

Up to now accurate rotational constants were determined for the fluorene molecule^{11,12} and the fluorene-Ar complex,¹¹ both from frequency and time domain measurements.¹³ However, presently no clear experimental information on the structure of fluorene-(Ar)₂ is available. In fluorene the transition dipole is directed along the *long*

in-plane axis. This is different from the situation in carbazole in which the transition moment is directed along the *short* in-plane axis. This leads to different rotational selection rules in the rovibronic transitions of the two monomers and the complexes with analogous structures.

II. EXPERIMENT

Fluorene (Fluka) vapor was produced at a pressure of 2 mbar in a heatable 20 cm³ chamber of a pulsed solenoid valve at 100 °C, seeded in a mixture of 2 bar Ne and 0.2 bar Ar and expanded through a 300 μm orifice into the vacuum chamber.

Low-resolution spectra were obtained by one-color resonance-enhanced two-photon ionization in a skimmed supersonic beam (skimmer with 1.5 mm diam) using a frequency-doubled broadband ($\Delta\nu_{UV}=0.3\text{ cm}^{-1}$) dye laser (Lambda Physik FL2002) operated with Coumarin 153 dye. The laser beam was not focused and care was taken to keep intensities below 10^5 W/cm^2 (100 μJ for a 10 ns pulse length and 10 mm² spot size). The ions were mass-selected in a home-built linear time-of-flight (TOF) mass spectrometer.

The experimental setup for recording of Doppler free high-resolution spectra of van der Waals molecules by mass-selected resonance-enhanced two-photon ionization has been described in our previous work.^{9,14,15} Briefly, for the narrow-band excitation step the single mode light of a cw dye laser (Coherent 699/21) is amplified in three amplifier stages pumped by a XeCl excimer laser (Lambda Physik EMG 201 MSC) yielding nearly Fourier transform limited 10 ns (FWHM) pulses. Since the fluorene-(Ar)_{*n*} transitions are located to the red of the wavelength range of our narrow-band laser system operating with Coumarin 102 dye, we used a special multipass narrow-band Raman shifter¹⁶ with low density H₂ gas to shift the laser frequency without loss of spectral selectivity. After frequency doubling the Raman shifted light with a resulting frequency width of 140 MHz (FWHM) was used for $S_1 \leftarrow S_0$ excitation of fluorene-(Ar)₂ in the frequency range around $33\,700\text{ cm}^{-1}$. In order to avoid saturation broadening in the high-resolution spectra, we attenuated the exciting narrow-band laser light to a pulse en-

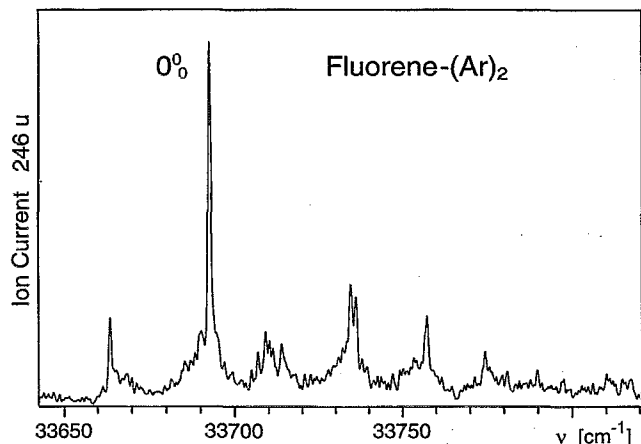


FIG. 1. Mass-selected low-resolution spectrum of fluorene-(Ar)₂ in the region of the $S_1 \leftarrow S_0$ origin transition, recorded with the one-color resonance-enhanced two-photon ionization technique.

ergy of 100 nJ for a 10 ns pulse length and 10 mm² spot size, which was below the minimum intensity to detect a resonance-enhanced one-color ion current. To achieve a detectable ion signal, we used a second strong, ionizing laser pulse (0.5 mJ for a 10 ns pulse length and 10 mm² spot size) with a fixed wavelength of 596 nm tuned to the red of the $S_1 \leftarrow S_0$ resonance. In this way a one-color background signal from this laser was avoided and fragmentation of the product cluster ions was minimized. The experimental resolution is determined by a convolution of the frequency width of the exciting light pulses ($\Delta\nu=140$ MHz) and the residual Doppler width of about 40 MHz.

III. RESULTS

A. Low-resolution spectrum

In Fig. 1 the mass-selected low-resolution spectrum around the 0_0^0 transition of fluorene-(Ar)₂ is shown, when recorded with the one-color resonance-enhanced two-photon ionization technique. The most intense feature (Fig. 1) is the $S_1 \leftarrow S_0$ (0_0^0) transition of the complex. The width of the bands is about 1 cm⁻¹ (FWHM) which is given by the width of the rotational contour under the expansion conditions of our experiment (see below). Thus the strongest feature is due to one rigid isomer whose structure is investigated in this work. The position of the strongest feature in the low-resolution spectrum is similar to that found in Ref. 2, however, some additional structure is resolved in the spectrum of this work. These weaker features in Fig. 1 are discussed in Sec. IV.

B. The structure of fluorene-Ar

Knowledge of the structure of the fluorene-Ar complex is helpful for the discussion of the structure of fluorene-(Ar)₂. The spectra of the bare fluorene molecule as well as of the fluorene-Ar van der Waals complex were measured by Meerts *et al.* in a high-resolution laser-induced fluorescence (LIF) experiment with cw lasers.¹¹ The experi-

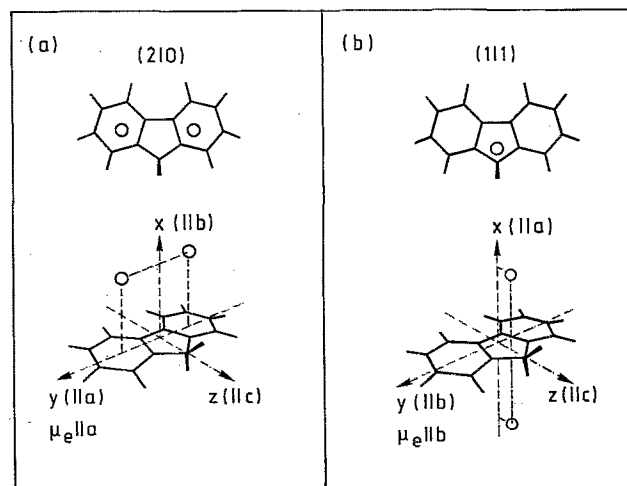


FIG. 2. $2|0$ structure of fluorene-(Ar)₂ (a), and one $1|1$ structure discussed in the text (b). The principal axis system (x, y, z) of the bare molecule is indicated together with the principal axes (a, b, c) of the complexes which are parallel displaced. The electronic transition dipole of fluorene μ_e is long-axis(y) polarized.

ments confirmed that the electric transition dipole moment μ_e is directed along the long in-plane axis of fluorene in the S_0 and S_1 states.^{3,17} The Ar atom was found to be placed above the central five-membered ring at an effective distance of 3.42 Å from the substrate plane and a slight parallel displacement of ± 0.53 Å from the center of mass of the bare molecule towards (or away from) the carbon atom located in the bisecting plane of the molecule.¹¹ This sign ambiguity results from the fact that the moments of inertia depend on the squares of the coordinates of the atoms.

C. The structure of fluorene-(Ar)₂: $2|0$ vs $1|1$

First we will investigate whether in the fluorene-(Ar)₂ complex both Ar atoms are attached on one side of the fluorene molecule, $2|0$ [see Fig. 2(a)] or one Ar atom on each side, $1|1$ [see Fig. 2(b)].

Fluorene-(Ar)₂ with a $2|0$ structure [see Fig. 2(a)] is an asymmetric prolate-like top ($\kappa=-0.456$) with the Ar atoms placed on the same side above the six-membered rings with the distance of 3.42 Å from the molecular plane found for fluorene-Ar¹¹ and an Ar-Ar distance of 3.76 Å as in the free Ar₂ dimer.¹⁸ In Fig. 2(a) the principal axis system of the bare molecule (x, y, z) and the resulting principal axis system (a, b, c) of the $2|0$ complex are indicated.

Now we calculate the typical rotational structure of the electronic $S_1 \leftarrow S_0$ origin band for a $2|0$ complex. As can be seen from Fig. 2(a) for a $2|0$ structure, the transition dipole, which is known from crystal data to be polarized along the long in-plane axis of fluorene,¹⁷ is an a -type transition moment. Thus we use a -type rotational selection rules of a prolate-like asymmetric top with $(ee) \leftrightarrow (eo)$ and $(oe) \leftrightarrow (oo)$ for (K_{-1}, K_{+1}) to calculate the rotational structure of the 0_0^0 transition of a $2|0$ complex. The effective principal moments of inertia I_a^C, I_b^C, I_c^C of a $2|0$ complex and the rotational constants in the electronic ground state are

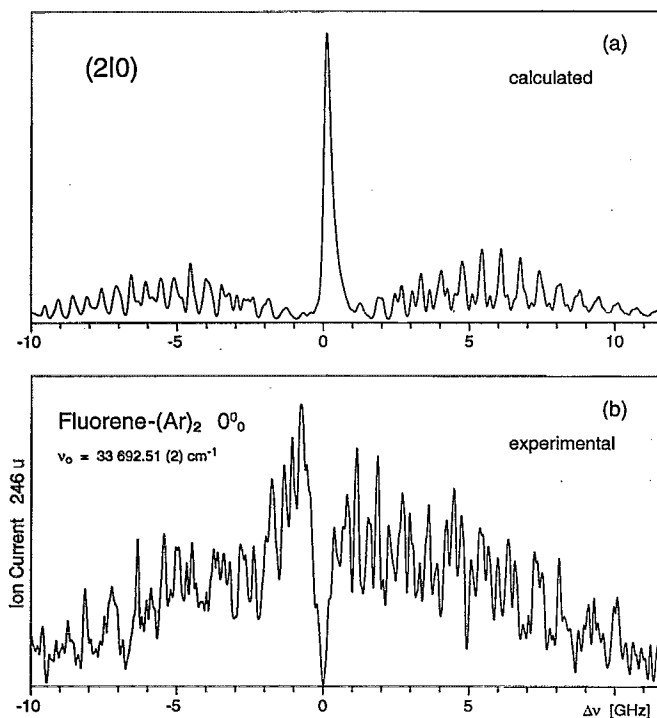


FIG. 3. (a) Theoretical rotational spectrum of the $S_1 \leftarrow S_0$ origin calculated for a $(2|0)$ structure of fluorene-(Ar) $_2$. (b) Experimental high-resolution spectrum of the $S_1 \leftarrow S_0$ origin band of fluorene-(Ar) $_2$.

calculated from the effective principal moments of inertia I_a^M, I_b^M, I_c^M of the bare molecule,¹¹ and the positions (in Å) of the two Ar atoms $(+3.42, +1.88, 0)$, $(+3.42, -1.88, 0)$ using Kraitchman's equations.^{19,20} We use

$$\begin{aligned} I_b^C &= I_c^M + 2my^2, \\ I_a^C &= I_a^M + 2\mu x^2, \\ I_c^C &= I_b^M + 2my^2 + 2\mu x^2 \end{aligned} \quad (1)$$

with $\mu = 2mM/(M + 2m)$. M is the molecular mass of fluorene in atomic units u , m is the atomic mass of Ar. Furthermore we use $I_a^C = h/8\pi^2 A_0''$, $I_b^C = h/8\pi^2 B_0''$, and $I_c^C = h/8\pi^2 C_0''$ defining effective moments of inertia. To find a guess of the changes of the rotational constants after electronic excitation a slight decrease of the van der Waals bond length as found for benzene-Ar,¹⁴ benzene-(Ar) $_2$,⁷ and *p*-difluorobenzene-Ar¹⁵ is assumed. In this way we obtain the rotational constants $A_0'' = 0.019\,59\text{ cm}^{-1}$, $B_0'' = 0.012\,20\text{ cm}^{-1}$, $C_0'' = 0.009\,44\text{ cm}^{-1}$ and $A_0' = 0.019\,79\text{ cm}^{-1}$, $B_0' = 0.012\,11\text{ cm}^{-1}$, $C_0' = 0.009\,54\text{ cm}^{-1}$ for calculation of the spectrum of the 0_0^0 band in fluorene-(Ar) $_2$, $(2|0)$ which is shown in Fig. 3(a). The theoretical spectrum displays the typical rotational structure of a parallel-type band with a sharp Q branch in the center and clearly separated P - and R -branch subgroups [see Fig. 3(a)]. Quite similar parallel-type bands are found for various $(2|0)$ structures [e.g., another plausible $(2|0)$ structure with the Ar atoms centrally occupying each of the phenyl rings], since all conceivable $(2|0)$ structures represent prolate-like asymmet-

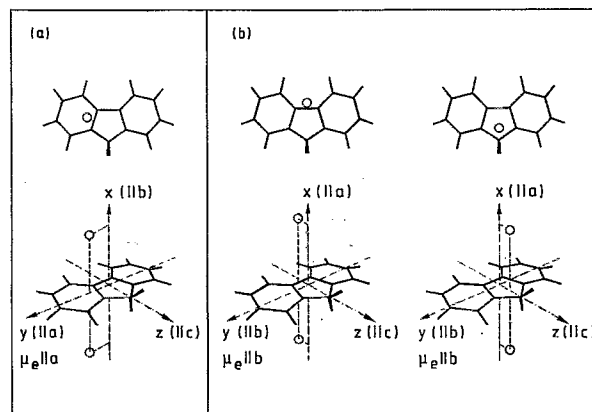


FIG. 4. Structure of fluorene-(Ar) $_2$ (b) found from experiment with only one remaining ambiguity in the z coordinate of the Ar atoms. Another chemical relevant structure (a) which can be excluded from experiment. The principal axis system (x, y, z) of the bare molecule is indicated together with the principal axes (a, b, c) of the complexes which are parallel displaced. The electronic transition dipole of fluorene μ_e is long-axis(y) polarized.

ric rotors with their a axis parallel to the transition dipole. As a result we find that the calculated parallel-type rotational structure in Fig. 3(a) is in striking disagreement with the experimentally observed rotational contour of fluorene-(Ar) $_2$ shown in Fig. 3(b). Thus we exclude the possibility that the band at $\nu_0 = 33\,692.51(2)\text{ cm}^{-1}$ is due to a one-sided $(2|0)$ structure of fluorene-(Ar) $_2$. It points to a $(1|1)$ structure of the complex in agreement with our recent result for carbazole-(Ar) $_2$.⁹

D. Specific $(1|1)$ structure of fluorene-(Ar) $_2$

After the exclusion of a $(2|0)$ structure of the complex we would like to derive the specific kind of $(1|1)$ structure from our experiment. In principle six different $(1|1)$ binding topologies of fluorene-(Ar) $_2$ are found for essentially the same set of ground-state rotational constants, with two different possible rotational transition types involved (see below). Among these, three different $(1|1)$ structures are chemically relevant and shown in Fig. 4. They are near oblate asymmetric rotors ($\kappa = +0.669$) with the unique axis being the $z(\parallel c)$ axis. The two structures shown in Fig. 4(b) with the Ar coordinates $(x, 0, z)$, $(-x, 0, z)$ or $(x, 0, -z)$, $(-x, 0, -z)$ are both described by exactly the same momental ellipsoid $(x\parallel a, y\parallel b, z\parallel c)$. The structure shown in Fig. 4(a) with the coordinates $(x, y, 0)$, $(-x, y, 0)$ has essentially the same momental ellipsoid. It is, however, rotated by 90° around the c axis $(x\parallel b, y\parallel a, z\parallel c)$ thus changing the rotational transition type from b -type to a -type.

Experiment allows to distinguish both types of transitions. To find a set of rotational ground-state constants for the simulation of the measured band structure we assume the position of the Ar atoms in the fluorene-(Ar) $_2$ complex [see Fig. 4(b)] to be the same as the Ar position in the fluorene-Ar complex (see Sec. III B). This is a reasonable assumption as we have shown for the case of benzene-Ar¹⁴ and benzene-(Ar) $_2$.⁷ With the coordinates (in Å) of the Ar

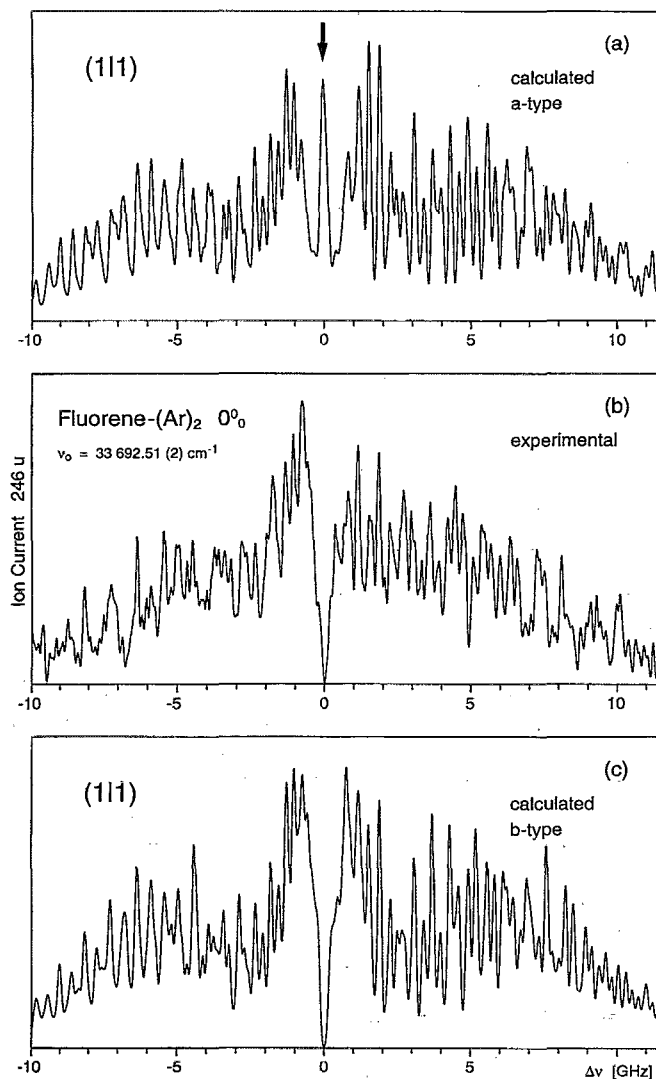


FIG. 5. (a) Rotational spectrum of the $S_1 \leftarrow S_0$ origin calculated for a (1|1) structure of fluorene-(Ar)₂ as shown in Fig. 4(a). The sharp Q branch is indicated by an arrow. (b) Experimental high-resolution spectrum of the $S_1 \leftarrow S_0$ origin band of fluorene-(Ar)₂. (c) Simulation of the experimental spectrum in (b) by a calculated spectrum. The assumed (1|1) structure is in line with the (1|1) structures shown in Fig. 4(b).

atoms (+3.42, 0, -0.53), (-3.42, 0, -0.53) or (+3.42, 0, +0.53), (-3.42, 0, +0.53) and the relations¹⁹

$$\begin{aligned} I_a^C &= I_c^M + \mu z^2 \\ I_b^C &= I_a^M + \mu z^2 + 2mx^2, \\ I_c^C &= I_b^M + 2mx^2 \end{aligned} \quad (2)$$

[μ defined in Eq. (1)], we find the following ground-state rotational constants of the complex $A_0'' = 0.015\ 24\ \text{cm}^{-1}$, $B_0'' = 0.014\ 27\ \text{cm}^{-1}$, $C_0'' = 0.009\ 38\ \text{cm}^{-1}$. They are numerically the same for all (1|1) structures discussed in Figs. 4(a) and 4(b). The experimental spectrum [see Fig. 5(b)] is satisfactorily reproduced [see Fig. 5(c)] with b -type rotational selection rules, a rotational temperature of 1.2 K, and

with the nuclear spin statistical weights for C_{2v} symmetry, $g_n = 496$ for $(K''_{-1}, K''_{+1}) = (ee)$ or (oe) and $g_n = 528$ for $(K''_{-1}, K''_{+1}) = (oo)$ or (eo) (e, o denotes the even or odd parity). The simulation yields excited state constants $A'_0 = 0.015\ 22\ \text{cm}^{-1}$, $B'_0 = 0.014\ 32\ \text{cm}^{-1}$, $C'_0 = 0.009\ 53\ \text{cm}^{-1}$ with a relatively low accuracy since the rotational line structure of the perpendicular band is not completely resolved. The electronic spectrum calculated from these rotational constants, and the a -type rotational selection rules of the binding topology of Fig. 4(a), is shown in Fig. 5(a). It is obvious that the sharp Q branch indicated in the center of the a -type spectrum of Fig. 5(a) does not fit the experimental spectrum of Fig. 5(b). Only the theoretical b -type spectrum of Fig. 5(c) matches the experimental contour. Thus we can exclude the structure of Fig. 5(a) with the two Ar atoms located above the benzene rings in a (1|1) structure. This is proof for the centrally bound (1|1) structure displayed in Fig. 4(b) with the only remaining ambiguity in the sign of the z coordinate.

E. Are there indications of other isomers?

After identification of the structure of the fluorene-(Ar)₂ complex with the 0_0^0 transition at $\nu_0 = 33\ 692.51(2)\ \text{cm}^{-1}$ we would like to address the question of whether an additional isomer with (2|0) structure exists. The 0_0^0 transition of the (2|0) isomer should display a smaller band shift than the (1|1) isomer since the strict additivity rule no longer holds.²¹ Thus, possible candidates for the origin transition of the (2|0) isomer should be located to the blue of the $33\ 692.51(2)\ \text{cm}^{-1}$ transition rotationally resolved in this work. The first feature [$33\ 711(3)\ \text{cm}^{-1}$] to the blue of the main feature in Fig. 1 is at least partially due to fragmentation of a larger complex since it can also be seen in the spectrum of fluorene-(Ar)₃.² We measured the transition at $\approx 42\ \text{cm}^{-1}$ to the blue [$33\ 734.6(1)\ \text{cm}^{-1}$] of the 0_0^0 transition of (1|1) fluorene-(Ar)₂ (see Fig. 1) with rotational resolution. It displays a rotational structure very similar to the rotational structure of the 0_0^0 transition at $33\ 692.51(2)\ \text{cm}^{-1}$. Thus it is clearly not due to a (2|0) isomer, which would display a parallel-type band [see Fig. 3(a)], and is therefore probably due to a totally symmetric van der Waals stretch vibration. This is reasonable as can be seen from a comparison of its frequency with the van der Waals stretch frequency in fluorene-Ar of $43.48(2)\ \text{cm}^{-1}$.¹⁰ Assuming a simple triatomic approximation²² we estimate a symmetric stretch frequency of $39\ \text{cm}^{-1}$ in the heterotrimer which is close to the observed frequency difference. Assuming a small anharmonicity we tentatively assign the feature at $33\ 774.5(1)\ \text{cm}^{-1}$ to the stretching overtone. The other bands [at $33\ 736.1(1)\ \text{cm}^{-1}$, $33\ 757.2(1)\ \text{cm}^{-1}$, and some smaller ones] are probably van der Waals vibronic bands of (1|1) fluorene-(Ar)₂, however, at present we cannot exclude that they are due to a (2|0) isomer. From the relative intensities of the different bands in Fig. 1 we deduce an upper limit for the relative abundance of a (2|0) isomer of 10%. Additional high-resolution experiments to address this question are in progress.

IV. SUMMARY AND CONCLUSIONS

In this work we present the first experimental determination of the structure of fluorene-(Ar)₂. It is clearly shown that the vibronic transition at 33 692.51(2) cm⁻¹ is due to a centrally bound opposite-sided (1|1) structure of fluorene-(Ar)₂. As discussed above one sign ambiguity remains, i.e., the question whether there is a slight displacement of both Ar atoms from the center towards the basis of the five-membered ring [(-z) direction] or towards the carbon atom on the vertical symmetry plane [(+z) direction]. In principle this ambiguity can be addressed using different isotopic species. However, this does not work for the fully deuterated species which is commercially available as has been shown for the case of the fluorene-Ar complex.²³ The argon (-z) position is likely because of the steric effect of the two hydrogen atoms located above and below the molecular plane.

In summary, a (1|1) structure was identified as the dominating structure for fluorene-(Ar)₂. A possible explanation for this would be the kinetics of the formation process⁴ or the influence of entropy effects²⁴ favoring the production of a (1|1) structure. Production of (n|0) (n=1-6) complexes (nonwetting) was concluded from molecular dynamics calculations for "bent" substrates like carbazole, dibenzofuran, etc.²⁵ It was shown theoretically that the probability for opposite-sided clusters (wetting behavior) increases with increasing cluster size because there is a higher probability for side crossing. As we find a higher probability for an opposite-sided structure already for the smallest unit, fluorene-(Ar)₂, this can be taken as an indication for preferred wetting behavior in case of larger fluorene-(Ar)_n complexes.

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- ¹A. Amirav, U. Even, and J. Jortner, *Chem. Phys.* **67**, 1 (1982).
- ²S. Leutwyler, U. Even, and J. Jortner, *J. Chem. Phys.* **79**, 5769 (1983).
- ³A. R. Auty, A. C. Jones, and D. Phillips, *Chem. Phys.* **103**, 163 (1986).
- ⁴S. M. Ohline, L. L. Connel, P. W. Joireman, V. A. Ventura, and P. M. Felker, *Chem. Phys. Lett.* **193**, 335 (1992).
- ⁵S. Leutwyler and J. Bösiger, *Chem. Rev.* **90**, 489 (1990).
- ⁶C. A. Haynam, D. V. Brumbaugh, and D. H. Levy, *J. Chem. Phys.* **80**, 2256 (1984).
- ⁷Th. Weber and H. J. Neusser, *J. Chem. Phys.* **94**, 7689 (1991).
- ⁸H. J. Neusser, R. Sussmann, A. M. Smith, E. Riedle, and Th. Weber, *Ber. Bunsenges. Phys. Chem.* **96**, 1252 (1992).
- ⁹R. Sussmann and H. J. Neusser, *Chem. Phys. Lett.* **221**, 46 (1994).
- ¹⁰H. J. Neusser and R. Sussmann, in *Jet Spectroscopy and Molecular Dynamics*, edited by J. M. Hollas and D. Phillips (Chapman and Hall, London, 1994).
- ¹¹W. L. Meerts, W. A. Majewski, and W. M. van Herpen, *Can. J. Phys.* **62**, 1293 (1984).
- ¹²J. F. Kauffman, M. J. Cote, P. G. Smith, and J. D. McDonald, *J. Chem. Phys.* **90**, 2874 (1989).
- ¹³J. S. Baskin and A. H. Zewail, *J. Phys. Chem.* **93**, 5701 (1989).
- ¹⁴Th. Weber, A. von Barga, E. Riedle, and H. J. Neusser, *J. Chem. Phys.* **92**, 90 (1990).
- ¹⁵R. Sussmann, R. Neuhauser, and H. J. Neusser, *Can. J. Phys.* (in press).
- ¹⁶R. Sussmann, Th. Weber, E. Riedle, and H. J. Neusser, *Opt. Commun.* **88**, 408 (1992).
- ¹⁷A. Bree and R. Zwarich, *J. Chem. Phys.* **51**, 903 (1969).
- ¹⁸P. R. Herman, P. E. LaRocque, and B. P. Stoicheff, *J. Chem. Phys.* **89**, 4535 (1988).
- ¹⁹W. Gordy and R. L. Cook, *Microwave Molecular Spectra*, 3rd ed. (Wiley-Interscience, New York, 1984), Chap. XIII.
- ²⁰A. Held and D. W. Pratt, *J. Am. Chem. Soc.* **112**, 8629 (1990).
- ²¹S. Leutwyler, *Chem. Phys. Lett.* **107**, 284 (1984).
- ²²G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1945), Vol. II, p. 154.
- ²³W. M. van Herpen and W. L. Meerts, *Chem. Phys. Lett.* **147**, 7 (1988).
- ²⁴R. S. Berry, J. Jellinek, and G. Natanson, *Phys. Rev. A* **30**, 919 (1984).
- ²⁵S. Leutwyler and J. Bösiger, *Faraday Discuss. Chem. Soc.* **86**, 225 (1988).