ELSEVIER

Chemical Physics Letters 221 (1994) 46–52

CHEMICAL PHYSICS LETTERS

Structure of the carbazole–Ar_2 trimer from high resolution UV spectroscopy

R. Sußmann, H.J. Neusser

Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany

Received 7 December 1993; in final form 3 February 1994

Abstract

Highly resolved spectra of the 0_0^0 ($S_1 \leftarrow S_0$) transition of the carbazole–Ar_2 complex were measured by mass-selective resonance-enhanced two-photon ionization with a narrow-band pulsed laser ($\Delta\nu < 140$ MHz). The parallel c-type rotational band structure displays regular sharp features which are used to find an accurate set of rotational constants of the trimer. From the experimental result a (2|0) structure of the investigated complex with the two Ar atoms located on one side of the carbazole plane can be excluded. Two possible (1|1) structures and consequences for the solvation mechanism are discussed.

1. Introduction

Carbazole–Ar_n clusters have been extensively used as model systems for the investigation of solute–solvent interactions [1]. Like benzene and other planar aromatic molecules carbazole can be understood as a microsurface for the growth of a rare-gas solvent cluster. Currently discussed questions are whether the solvent cluster spreads like a film on both sides of the aromatic substrate (wetting behavior), or forms a droplet-like substructure on one side (nonwetting) [1–3].

The smallest possible systems for which a wetting–nonwetting behavior can occur are aromatic molecules soluted by two solvent atoms. For systems of this size accurate spectroscopic structural information is within the realm of possibility. Mass-selective resonance-enhanced two-photon ionization with narrow-band pulsed lasers yielded highly accurate van der Waals bond lengths of benzene–rare-gas complexes [4–6]. In particular, the rotationally resolved UV spectrum of the most abundant benzene–Ar_2 isomer proves the (1|1) structure of the complex, i.e. both argon atoms are located symmetrically above the plane on both sides of the molecule [7,8]. The existence of a less abundant (2|0) isomer with both argon atoms attached on one side of the molecule was concluded from a low resolution rotational contour [9], however, its proof by high resolution rotationally resolved spectroscopy is still missing. The high resolution UV spectroscopy of *s*-tetrazine–rare-gas trimers demonstrated a (1|1) structure of (amino)-*s*-tetrazine–Ar_2 [10,11]. Microwave spectra of furan–Ar_2 [12] and Ne-benzene–H_2O [13] gave proof of a (1|1) structure. On contrary, rotational contour analysis of low resolution vibronic spectra of benzene–$(H_2O)_2$ pointed to a (2|0) structure as a result of the strong hydrogen bonding between the water molecules on one side of the ring [14,15]. The carbazole–Ar_n system has been investigated by mass selective vibronic spectroscopy with low resolution [1,16]. Monte Carlo and molecular dynamics simulations based on empirical 6–12 potentials were used to interpret the spectroscopic results. One of the con-

0009-2614/94/$07.00 © 1994 Elsevier Science B.V. All rights reserved
SSDI 0009-2614(94)00224-E

clusions of this work was that complexes with an Ar atom number $n<7$ display $(n|0)$ structures, i.e. the Ar atoms solvate only on one side of the carbazole surface. In particular, the vibronic transition at 30720 cm^{-1} in carbazole–Ar_2 was assigned to a $(2|0)$ structure of carbazole–Ar_2 trimers [1,16]. Recently, using the method of time-resolved rotational coherence spectroscopy, Felker and co-workers presented experimental evidence for a $(1|1)$ structure of carbazole–Ar_2 [17]. Rotational coherence spectroscopy yields linear combinations of two rotational constants of the excited electronic state (A' and B') in a direct way without the complicated analysis necessary in rotationally resolved UV spectroscopy in the frequency domain. From time domain measurements values for $A'+B'$ and $A'-B'$ were derived with an uncertainty of $\pm 0.5\%$ and $\pm 15\%$, respectively [17] and there was no possibility to determine the third rotational constant C' for this parallel-type transition.

In this work we present new data on the carbazole–Ar_2 complex which support the results from rotational coherence spectroscopy [17]. The high resolution UV spectroscopy performed in this work yields rotational contours with clear microstructure. It is used to determine the rotational constants of the complex with hithertho unachieved accuracy, and the resulting possible structures are discussed.

2. Experimental

We investigated the carbazole–Ar_2 complex measuring the origin of the near-UV $\pi\pi^*$ electronic transition ($^1A_1 \leftarrow {}^1A_1$) of its chromophore, carbazole, with point group C_{2v}. This origin is shifted by about 90 cm^{-1} to the red of the respective transition in the carbazole monomer. The transition dipole moment of the monomer between the totally symmetric ($^1A_1$) S_0 and S_1 electronic states is polarized along the carbazole short in-plane axis [18]. The experimental setup for recording of high resolution UV spectra of cluster molecules by mass-selected resonance-enhanced two-photon ionization is shown in Fig. 1. Its main components are described in earlier work on high-resolution rotationally resolved spectroscopy of benzene–Ar [4]. The frequency of the carbazole–Ar_2 transition is to the red of the frequency range of our narrow-band laser system operating with coumarin 307 dye in the amplifier stages. Therefore we used a

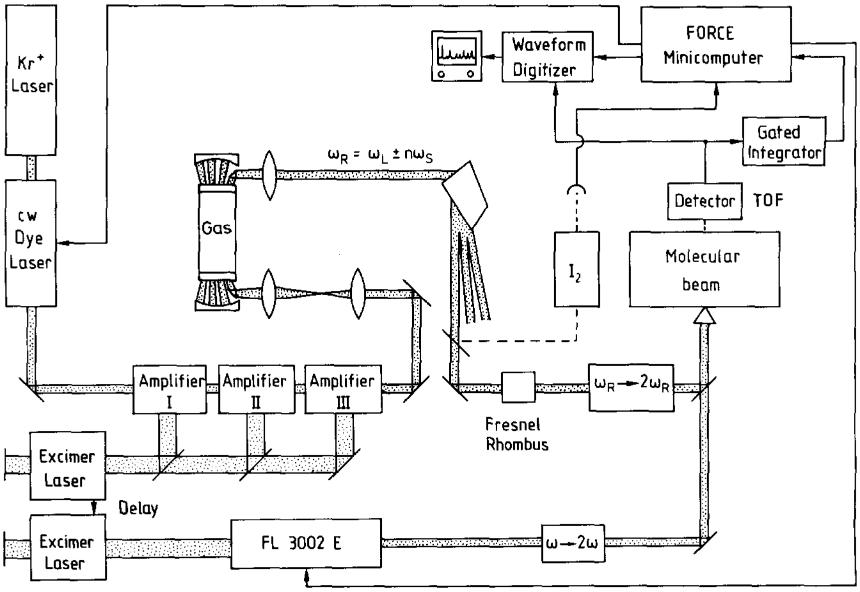

Fig. 1. Experimental setup for the recording of high resolution UV spectra by mass-selective resonance-enhanced two-photon ionization in a skimmed supersonic beam. To reach the frequency range of carbazole–Ar_2 a narrow-band multipass Raman shifter is employed [19].

special multipass narrow-band Raman shifter [19], operating with low density H_2 gas (3.5 amagat) as a Raman medium, to shift the laser frequency by 4155.235(10) cm^{-1} from 19515 to 15360 cm^{-1} without loss of spectral selectivity. After frequency doubling the Raman-shifted light with a frequency width of 140 MHz was used for the excitation of carbazole–Ar_2. Because of its low vapor pressure carbazole (Fluka) was heated up to 160°C yielding a vapor pressure of 0.5 mbar. It was seeded in a mixture of 2 bar Ne and 0.2 bar Ar and expanded into the vacuum chamber through a home-made heatable solenoid valve with 300 μm orifice.

In carbazole the S_1 intermediate state is halfway to the ionization energy. Consequently in previous work low resolution intermediate state spectra of complexes were measured in a one laser experiment [1,16]. The absorption of a second photon of the same color results in a small excess energy of the ionized complexes and does not lead to their dissociation. In high resolution spectroscopy we found that one-color excitation leads to saturation broadened spectra: Since ionization close above threshold is not efficient high laser intensities (100 μJ for a 10 ns pulse length and 10 mm^2 beam diameter) are needed leading to a broadening of the first $S_1 \leftarrow S_0$ excitation step with a relatively large oscillator strength of $f = 0.042$. To record the rotationally resolved spectrum of carbazole–Ar_2 without broadening we used two lasers. The strong broadband ionizing laser pulse (0.5 mJ for a 10 ns pulse length and 10 mm^2 beam diameter) was fixed at a wavelength slightly to the red of the $S_1 \leftarrow S_0$ resonance to avoid a one-color background signal from this laser. The narrow-band laser system providing the photon for the first excitation step was attenuated to a pulse energy of 100 nJ. This pulse energy is three orders of magnitude smaller than the minimum value of 100 μJ necessary for a detectable one-color signal (see above).

3. Results and discussion

3.1. Spectrum

The spectrum shown in the upper trace of Fig. 2 resulted when recording the ion current at 247 u as a function of the exciting narrow-band laser frequency.

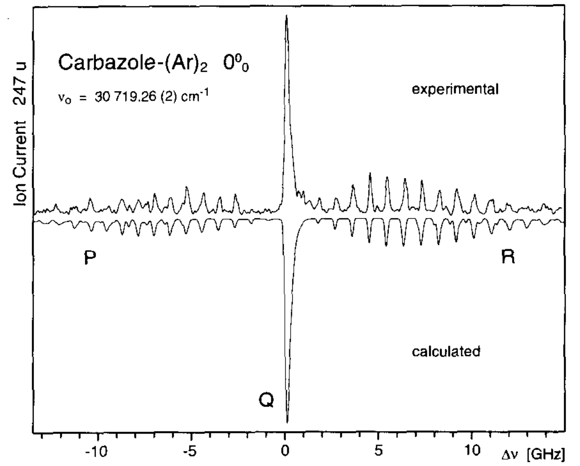

Fig. 2. Upper trace: Mass-selective high resolution UV spectrum of the 0^0_0 ($S_1 \leftarrow S_0$) transition of carbazole–Ar_2. Lower trace: Calculated c-type rotational contour of a near-oblate asymmetric top calculated with the best set of rotational constants obtained from a fit of the rotational features in the experimental spectrum.

The spectral resolution of 150 MHz is mainly given by the width of the Raman-shifted light. The clearly defined P-, Q-, and R-branch structure in the band is characteristic of a parallel-type transition [20]. To analyze the rotational structure we used an asymmetric rotor program [21]. First tentative spectral assignments were made by comparison of the measured spectrum with spectra calculated from sets of rotational constants of guessed structures of the complex. The simulated spectra were then stepwise adjusted to the measured spectrum by comparing (i) the width and the shape of the Q-branch, (ii) the position of about 30 well separated narrow peaks resulting from P- and R-branch subgroups of rotational lines in the wings of the spectrum, and (iii) the relative intensities of these features. The calculated spectrum in the lower trace of Fig. 2 represents the best fit to the experimental spectrum. It is a c-type spectrum of a near-oblate ($\kappa = 0.693$) asymmetric top with selection rules (ee)↔(oe) and (eo)↔(oo) for (K_{-1}, K_{+1}), (e, o denotes the even and odd parity, respectively). Such as in the bare molecule, the transition dipole moment is polarized along the carbazole short in-plane axis. The nuclear spin statistical weights for C_{2v} symmetry are $g_n = 136$ for $(K''_{-1}, K''_{+1}) =$ (ee) or (oe) and $g_n = 120$ for $(K''_{-1}, K''_{+1}) =$ (eo) or (oo). Since both values do not differ too much, the effect of nuclear spin statistics on the line intensities is smaller than the experimental uncertainty in the peak intensities of 10%. The rotational temperature was found to be 1.5±0.5 K. From the simulated spectrum which was obtained after a 150 MHz (fwhm) Gaussian convolution of the calculated stick spectrum, we obtained the rotational constants $A_0''=0.01530(10)$ cm^{-1}, $B_0''=0.01444(20)$ cm^{-1}, $C_0''=0.0097(30)$ cm^{-1}, $\Delta A=A_0'-A_0''=-0.00015(5)$ cm^{-1}, $\Delta B=+0.00031(5)$ cm^{-1}, and $\Delta C=+0.00004(1)$ cm^{-1} and the wavenumber of the rotationless transition $\nu_0=30719.264(21)$ cm^{-1}. The constants A_0' and B_0' of ref. [17] agree with the values of this work within the error bars. The constants C_0'', C_0' are determined for the first time, however, with a relatively large error. This is a principle problem in the analysis of a c-type spectrum of a near-oblate asymmetric rotor.

3.2. Structure

From the rotational constants we are able to deduce the structure of the carbazole–Ar$_2$ complex and to distinguish whether both Ar atoms are attached on one side of the carbazole plane (2|0) or one Ar atom on each side (1|1).

For the following considerations we assume that both solvent Ar atoms are only a weak perturbation of the parent molecule, and the structure of the carbazole subunit in carbazole–Ar$_2$ is identical to the geometry of the bare carbazole monomer. This assumption is reasonable for the weak van der Waals forces between carbazole and Ar. The geometry of the complex is deduced using Kraitchman's method [22]. Initially this was a method for calculation of the position of one (or several) atom(s) in a molecule utilizing the changes in moments of inertia resulting from a single (or multiple) isotopic substitution of the atom(s). Here we make use of the fact that the method works in the same way, whether an atom is substituted or new one is added. The latter is the situation in our case where the positions of addatoms in a solute–solvent complex are to be determined. The (nondiagonal) moment of inertia tensor of the carbazole–Ar$_2$ complex ($\mathbf{I}^{\mathrm{C}}_{\mathrm{nd}}$) is derived from the moments of inertia of the monomer (I_x^M, I_y^M, I_z^M) along its principal axes and the positions of the argon atoms (x, y, z) in the principal axis system of the bare carbazole molecule which is defined in Fig. 3. A diagonalization of $\mathbf{I}^{\mathrm{C}}_{\mathrm{nd}}$ leads to the principal moments of inertia of the complex ($I_x^{\mathrm{C}}, I_y^{\mathrm{C}}, I_z^{\mathrm{C}}$) as a function of $I_x^{\mathrm{M}}, I_y^{\mathrm{M}}, I_z^{\mathrm{M}}$ of the monomer. The eigenvectors reflect whether a rotation of the principal axis system relative to that of the monomer occurs. Kraitchman's equations yield expressions for the coordinates $|x|$, $|y|$, and $|z|$ of substituted (or added) atoms in terms of the principal moments $I_x^{\mathrm{M}}, I_y^{\mathrm{M}}, I_z^{\mathrm{M}}$ (prior to substitution) and $I_x^{\mathrm{C}}, I_y^{\mathrm{C}}, I_z^{\mathrm{C}}$ (after substitution). The general ambiguity in the sign of the calculated coordinates results from the moments of inertia depending on the square of the coordinates of the atoms. Solutions were given for single and multiple substitutions in a variety of topological cases [23]. In order to find the appropriate Kraitchman equations all possible principle topologies of carbazole–Ar$_2$ trimers must be found that are consistent with the type of the observed rotational spectrum. Observing a parallel c-type rotational contour we have to search for near-oblate trimer topologies with the c axis parallel to the transition moment, i.e. parallel to the z axis in Fig. 3. We found that these preconditions were matched only for the geometries depicted in Figs. 3a and 3b. These structures can be described by the same momental ellipsoid with the only differ-

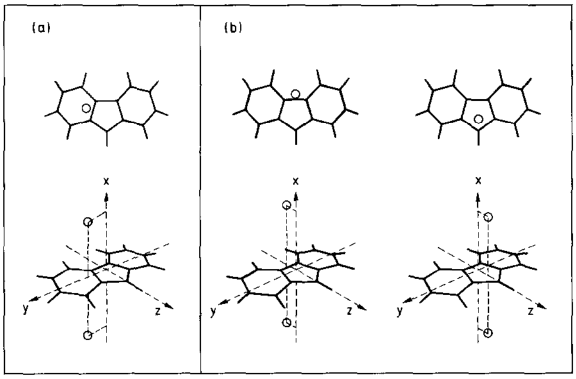

Fig. 3. Possible structures of carbazole–Ar$_2$ which are in line with the rotational constants derived from the high resolution UV spectrum of Fig. 2. The indicated coordinate system (x, y, z) is the principal axis system of the bare carbazole molecule. (a) (1|1) Structure with C$_s$ symmetry. The principal axes a, b, c of this structure are parallel to the monomer principal axes with $a \| y$, $b \| x$, $c \| z$. (b) Two different (1|1) structures with C$_{2v}$ symmetry. The principal axes of both structures are parallel to the monomer principal axes with $a \| x$, $b \| y$, $c \| z$. For the coordinates of the Ar atoms, see text.

ence that the *a* and *b* principal axes are interchanged for the structures of Figs. 3a and 3b, respectively. The detailed coordinates for these structures will be derived below.

Already at this point we can exclude a (2|0) structure which was claimed in refs. [1,16]. In this former work both Ar atoms were assumed to be placed on the same side of the carbazole surface with a distance of 3–4 Å and each Ar atom located above one of the six-membered rings of carbazole with a resulting Ar–Ar distance close to the spacing in the free Ar_2 dimer of 3.76 Å. The evaluation of the moment of inertia ellipsoid of this (2|0) structure yields a very asymmetric prolate top with its *a* axis parallel to the *y* axis of Fig. 3. Because the transition dipole moment is polarized along the *z* axis in Fig. 3 this would not lead to a parallel-type transition, i.e. the rotational structure would be completely different from the striking substructure of the P- and R-branches in Fig. 2 characteristic of a parallel-type transition. This was checked explicitly by calculation of the rotational contours of (2|0) structures with various sets of rotational constants.

After the exclusion of a (2|0) structure we would like to discuss possible (1|1) structures which are in line with our experimentally determined rotational constants (Fig. 3). The Ar coordinates of the first structure with C_s symmetry and a *yz*-symmetry-plane are $(x, y, 0)$ and $(-x, y, 0)$, respectively, in the center-of-mass system of carbazole (Fig. 3a). The axes *a*, *b*, *c* of the complex are parallel to the axes *y*, *x*, *z*, respectively, in Fig. 3. Since $z=0$, only two moments of inertia are needed for the calculation of *x* and *y*. We choose the moments of inertia corresponding to the constants A''_0 and B''_0 of the complex as their accuracy is higher than for C''_0. The resulting values for *x*, *y*, *z* (in Å) in the center-of-mass system of carbazole are

$$|x|=\left(\frac{\Delta I_y}{2m}\right)^{1/2}, \quad |y|=\left(\frac{\Delta I_x}{\mu}\right)^{1/2}, \quad |z|=0, \qquad (1)$$

where

$$\mu=\frac{2mM}{M+2m},$$

with $\Delta I_x = I_x^C - I_x^M$, etc. *M* is the molecular mass of carbazole in atomic units u, *m* is the atomic mass of argon. We calculated I_x^M, I_y^M, I_z^M (in u Å^2) from the crystal structure of carbazole given in ref. [24]. I_x^C, I_y^C, I_z^C were calculated from the experimentally determined rotational constants of the complex using the relations $I_x^C=h/8\pi^2B''_0$, $I_y^C=h/8\pi^2A''_0$, and $I_z^C=h/8\pi^2C''_0$, yielding effective moments of inertia that do not contain corrections for zero-point vibrational effects. In order to estimate the errors in the calculated Ar positions several sources for errors have to be considered. (i) The error resulting from the crystal structure of carbazole which may differ from its gas phase structure has been shown to be in the order of 1% for I_x^M, I_y^M, I_z^M in the similar case of fluorene [25]. Origins of this error are structure distortions in the crystal on one hand and the error of moments of inertia which are calculated from gas phase rotational constants with vibrational averaging. (ii) For an estimate of the accuracy of the determined moments of inertia I_x^C, I_y^C, I_z^C of the complex the experimental errors of the rotational constants were taken into account. (iii) The influence of vibrational averaging on the accuracy of the derived complex structure could be estimated replacing Eq. (1) by analogous equations containing I_z^C (corresponding to C''_0). This would yield slightly different coordinates. Unfortunately this is not reasonable in our case because of the low accuracy of C''_0 (see above). As a result for the Ar positions we found $|x|=3.31(2)$ Å, $|y|=1.38(10)$ Å, $|z|=0$, with the indicated uncertainties resulting from the errors in the experimentally determined rotational constants of the complex. In Fig. 3a the structure (+3.31 Å, 1.38 Å, 0) and (−3.31 Å, 1.38 Å, 0) for the coordinates of the Ar atoms is shown. The other possible structure (+3.31 Å, −1.38 Å, 0) and (−3.31 Å, −1.38 Å, 0) is not shown explicitly since it can be obtained by rotation of the structure in fig. 3a by 180°.

The second complex structure (Fig. 3b) with (x, y, z) and $(-x, -y, z)$ coordinates of the two Ar atoms is an oblate asymmetric rotor only if $y \ll x$, and $x \approx 3$–4 Å. For the calculation of *x*, *y*, *z* general Kraitchman equations, including three moments of inertia both of the complex and of the bare molecule must be applied. It results that $y=0$, i.e. a complex with C_{2v} symmetry, with the *z* axis as the C_2 axis. By fixing $y=0$ the Ar coordinates x and z are calculated from the two moments of inertia I_x^C and I_y^C resulting from the constants A_0'' and B_0'' of the complex:

$$|x| = \left(\frac{\Delta I_y - \Delta I_x}{2m}\right)^{1/2}, \quad |y| = 0, \quad |z| = \left(\frac{\Delta I_x}{\mu}\right)^{1/2}. \qquad (2)$$

Using $I_x^C = h/8\pi^2 A_0''$, $I_y^C = h/8\pi^2 B_0''$, and $I_z^C = h/8\pi^2 C_0''$ with $(a, b, c) \to (x, y, z)$ we found $|x| = 3.37(5)$ Å, $|y| = 0$, $|z| = 0.83(10)$ Å, for the coordinates of the two argon atoms. Because of the ± sign ambiguity the two different structures depicted in Fig. 3b where both argon atoms have either positive or negative z coordinates result.

In principle the three structures of carbazole–Ar_2 which are formally in line with the measured rotational constants and shown in Fig. 3 can be distinguished using different isotopic species of carbazole. However, this does not work for the fully deuterated species which is commercially available as has been shown for the similar case of the fluorene–Ar dimer [26]. Partially isotopically labelled carbazole samples are difficult to synthesize. Thus we have to look for other arguments supporting one of the structures in Fig. 3. A strong argument corroborating the (1|1) structures of Fig. 3b results from the situation in fluorene–Ar where the argon is located above the central five-membered ring [25]. Clear arguments supporting one of the structures shown in fig. 3a or 3b can be found in the analogous case of fluorene–Ar_2 where the transition dipole moment is polarized along the molecule's long in plane axis (analogous to the y axis in Fig. 3). Since the only difference between the structures in Figs. 3a and 3b is that the a and b axes are interchanged, structures of fluorene–Ar_2 like the one of Fig. 3a would display an a-type rotational spectrum while those of Fig. 3b would lead to a b-type spectrum. High resolution experiments on fluorene–Ar_2 are in progress to distinguish both discussed structures [27].

4. Summary and conclusion

In this work we presented the first high resolution UV spectrum ($\Delta\nu < 150$ MHz) of a molecule-noble-gas trimer with an aromatic (three ring) molecule of this size. The results presented above clearly indicate, that the experimentally observed peak at 30719.264(21) cm^{-1} originates from the 0_0^0 transition of carbazole–Ar_2 trimers with (1|1) rather than (2|0) structure. This result is in line with the observed bandshift of 88.88(4) cm^{-1} which is almost twice the bandshift of 45.87(4) cm^{-1} we determined for carbazole–Ar from its rotationally resolved UV spectrum. In our previous work on benzene–Ar_2 [7] we demonstrated that a clearly identified (1|1) structure is correlated with an additivity rule of the bandshift, which is in line with the investigations on (amino)-*s*-tetrazine–Ar_2 in refs. [10,11]. Carbazole–Ar_2 is a third example for this rule which holds strictly only for the solvation of noble-gas atoms in equivalent positions, i.e. noble-gas atoms in identical positions on opposite sides of the aromatic molecule.

The result that the (1|1) structure corresponds to the strongest vibronic feature in the UV spectrum is surprising in terms of energetic considerations since molecular dynamics calculations lead to a more stable (2|0) structure [1,16]. As has been pointed out in ref. [17] there are two apparent reasons for this discrepancy: Either the pairwise atom–atom potential used in refs. [1,16] is not adequate for this model system, and/or the kinetic process of cluster formation could account for the observed discrepancy favoring the formation of the (1|1) trimer by attachment of an Ar atom to a carabazole–Ar dimer. A similar effect was discussed in the case of benzene–Ar_n. There the energetic stability of opposite sided isomers does not preclude the formation of energetically less stable one sided isomers [3].

Whether the second isomer with (2|0) structure exists in lower abundance is not yet clear for carbazole–Ar_2. The 0_0^0 bandshift of the (2|0) isomer is expected to be smaller than the bandshift of the (1|1) isomer due to the interaction of both Ar atoms located on one side of the aromatic molecule, i.e. the 0_0^0 transition of the (2|0) isomer should be located to the red of the monomer transition and to the blue of the 30719.264 cm^{-1} transition of the (1|1) isomer discussed above. The spectrum in this region was investigated under low resolution and assigned to van der Waals vibronic bands [16]. From this one would exclude the existence of a second isomer with the structure proposed by Leutwyler and Bösiger [1,16]. However, this assignment was based on the assumption of a (2|0) structure, and the features at +15.6, +31.1 and +44.6 cm^{-1} to the blue of the 0_0^0 transition at 30719.264 cm^{-1} have to be reassigned. Rotationally resolved spectra of the vibronic features in this region will provide new information.

From the result presented in this work we expect a (2|1) structure for the carbazole–Ar_2 complex rather than the (3|0) structure favored in refs. [1,16]. This would bring about new arguments for discussion of solvation phenomena. The accurate investigation of this larger complexes with the technique of rotationally resolved UV spectroscopy is subject of future experiments.

Acknowledgement

The authors are indebted to Professor E.W. Schlag for his permanent interest in this work. They thank U. Zitt for his assistance during the course of the experiments. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] S. Leutwyler and J. Bösiger, Chem. Rev. 90 (1990) 489.
[2] N. Ben-Horin, U. Even and J. Jortner, Chem. Phys. Letters 188 (1992) 73.
[3] M. Schmidt, M. Mons and J. Le Calvé, Chem. Phys. Letters 177 (1991) 371.
[4] Th. Weber, A. von Bargen, E. Riedle and H.J. Neusser, J. Chem. Phys. 92 (1990) 90.
[5] Th. Weber, E. Riedle, H.J. Neusser and E.W. Schlag, J. Mol. Struct. 249 (1991) 69.
[6] Th. Weber, E. Riedle, H.J. Neusser and E.W. Schlag, Chem. Phys. Letters 183 (1991) 77.
[7] Th. Weber and H.J. Neusser, J. Chem. Phys. 94 (1991) 7689.
[8] H.J. Neusser, R. Sussmann, A.M. Smith, E. Riedle and Th. Weber, Ber. Bunsenges. Physik. Chem. 96 (1992) 1252.
[9] M. Schmidt, M. Mons, J. Le Calvé, P. Millié and C. Cossart-Magos, Chem. Phys. Letters 183 (1991) 69.
[10] C.A. Haynam, D.V. Brumbaugh and D.H. Levy, J. Chem. Phys. 80 (1984) 2256.
[11] J.C. Alfano, S.J. Martinez III and D.H. Levy, J. Chem. Phys. 94 (1991) 1673.
[12] R.M. Spycher, P.M. King and A. Bauder, Chem. Phys. Letters 191 (1992) 102.
[13] E. Arunan, T. Emilsson and H.S. Gutowsky, J. Chem. Phys. 99 (1993) 6208.
[14] A.J. Gotch, A.W. Garrett, D.L. Severance and T.S. Zwier, Chem. Phys. Letters 178 (1991) 121.
[15] A.J. Gotch and T.S. Zwier, J. Chem. Phys. 96 (1992) 3388.
[16] S. Leutwyler and J. Bösiger, Z. Physik. Chem. 154 (1987) 31.
[17] S.M. Ohline, L.L. Connel, P.W. Joireman, V.A. Venturo and P.M. Felker, Chem. Phys. Letters 193 (1992) 335.
[18] A.R. Auty, A.C. Jones and D. Phillips, Chem. Phys. 103 (1986) 163.
[19] R. Sussmann, Th. Weber, E. Riedle and H.J. Neusser, Opt. Commun. 88 (1992) 408.
[20] G. Herzberg, Molecular spectra and molecular structure, Vol. 3 (Van Nostrand, Princeton, 1967).
[21] H. Sieber, E. Riedle and H.J. Neusser, Chem. Phys. Letters 169 (1990) 191.
[22] J. Kraitchman, Am. J. Phys. 21 (1953) 17.
[23] W. Gordy and R.L. Cook, Microwave molecular spectra, Vol. 13, 3 rd Ed. (Wiley-Interscience, New York, 1984).
[24] M. Kurahashi, M. Fukuyo, A. Shimada, A. Furusaki and I. Nitta, Bull. Chem. Soc. Japan 42 (1969) 2174.
[25] W.L. Meerts, W.A. Majewsky and W.M. van Herpen, Can. J. Phys. 62 (1984) 1293.
[26] W.M. van Herpen and W.L. Meerts, Chem. Phys. Letters 147 (1988) 7.
[27] R. Sussmann, U. Zitt and H.J. Neusser, to be published.