Structure and Dynamics of Weakly Bound
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SPECTROSCOPY IN THE VISIBLE AND NEAR ULTRAVIOLET REGION OF SOME ORGANIC MOLECULES AND THEIR VAN DER WAALS COMPLEXES

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ABSTRACT. By using a molecular beam apparatus with a single frequency dye laser we were able to resolve several rovibronic transitions of some large molecules and their Van der Waals complexes with noble gas atoms. The rotational constants of tetracene, fluorene and the fluorene-argon complex have been determined. The structure of the complex was derived. In the rotational spectra of the tetracene-noble gas complexes perturbations were shown to be present, increasing with the size and number of the attached atoms. Fluorescence excitation spectra of trans-stilbene and the stilbene-argon complex are reported.

1. INTRODUCTION

Detailed spectroscopic information is indispensible in the study of Van der Waals (VdW) molecules. In recent years, much attention has been focussed on the understanding of structure, dynamics and energetics of small VdW complexes. Experimental data allow for realistic description of potential energy surfaces and relaxation phenomena. For larger complexes the density of states increases rapidly and so does the complexity of its spectra. Less information is therefore available on these molecules and model calculations lack of experimental verification. The insight on potential surfaces and solvent effects is rather limited.

To obtain experimental information on the structure of the complexes one needs rotationally resolved spectra. If single-frequency lasers are used, spectral resolution is limited by the Doppler-width of the spectral lines. One can either use Doppler-free techniques in cell experiments [1] or use a free jet expansion. With such an expansion and by strongly collimating the molecular beam the experimental linewidth can be reduced to a few MHz in the visible region. The seeded beam technique adds the advantage of a considerable cooling of internal degrees of freedom of the molecule. Moreover, the high density of VdW complexes in the beam of the parent molecule with the seeding gas is very convenient.

We report the high resolution spectroscopy of three large molecules and their VdW complexes with rare gas (R) atoms. Fluorescence excitation spectra have been obtained of fluorene (F), tetracene (T) and trans-stilbene (tS). The rotational constants of both F and the F-Ar complex have been determined in ground and excited electronic state. From this the structure of the F-Ar complex has been deduced and compared with model calculations. Rotational bands of T were also assigned. For the T-Ar, T-Kr and T-Xe VdW complexes perturbations in the excited state were shown to exist, depending on energy and size of the attached rare gas atom. The tS molecule shows complicated rovibronic spectra. Isomerisation in the excited state and internal rotation will be heavily influenced in a VdW complex. The observed bands of the tS-Ar complex are quite different from those of the tS parent molecule. This is attributed to the steric effect of the Ar-atom in the complex.

2. EXPERIMENTAL

In our studies on large molecules and their VdW complexes we applied the seeded beam technique. A detailed description of the apparatus can be found elsewhere [2,3]. The source (figure 1) of the molecular beam is made of quartz. It is wrapped with heating wires. Together with a

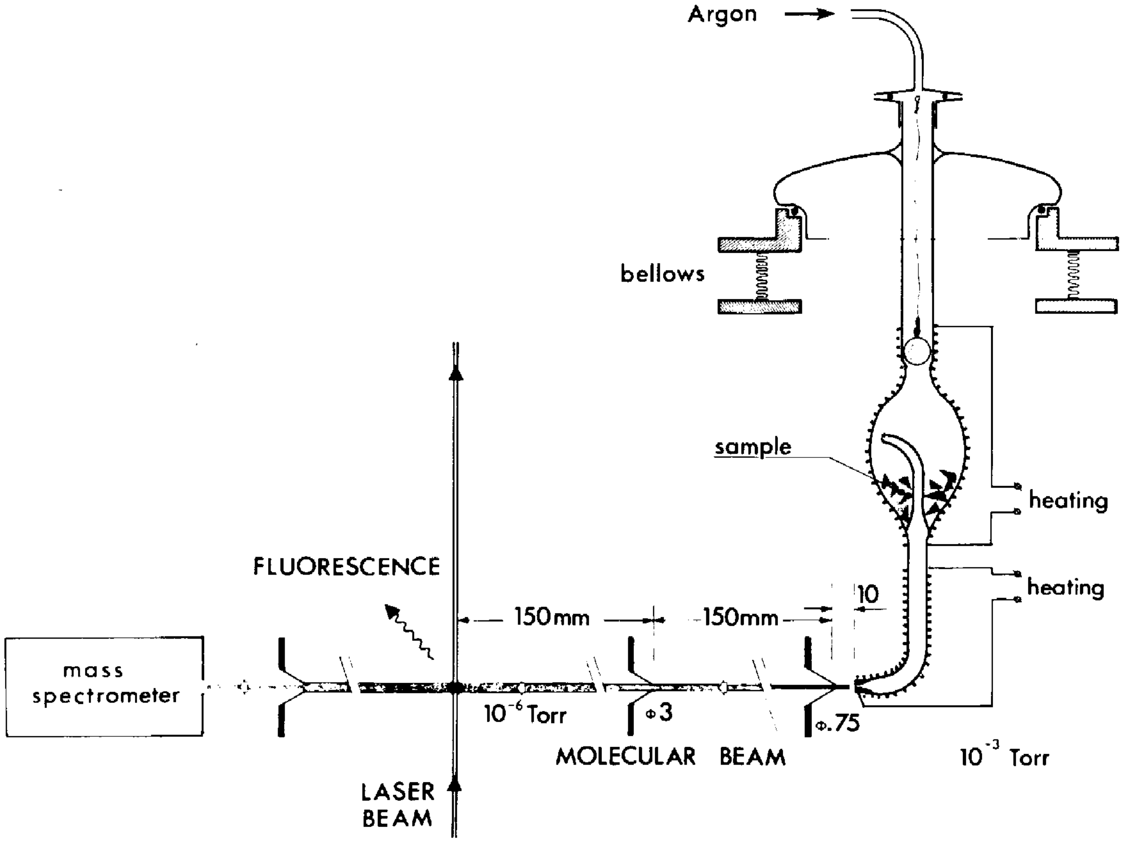

Figure 1. Schematic view of the source and molecular beam.

few thermocouples this allows temperature control of the source. The sample is heated in a reservoir compartment to raise its vapour pressure to typically 1 Torr. A mixture of the vapour and the seeding gas is expanded (at a pressure ranging up to 4 bar) by a circular nozzle of 100 μm diameter. Two conical skimmers in a two-step pumping system are used to collimate the molecular beam. This results in a residual Doppler width of about 15 MHz at UV wavelengths. The interaction zone with the laser is at 30 cm from the beam orifice. Here, the undispersed LIF is imaged to the photocathode of a photomultiplier tube (EMI 9863QA). To suppress background signal from scattered laser light, the molecular beam is chopped and phase sensitive detection is applied. We used a standard photon counting system, interfaced with a computer (PDP11/23 plus). The computer largely expands the dynamic range of the stored data. In the analysis accurate corrections can be made for nonlinearity in the scan. Moreover, the computer facilitates the tedious determination of position and intensities of the numerous spectral lines.

For the experiments described in this paper, we applied two different laser systems. The measurements on tetracene were performed with a standing wave linear dye laser (Coherent Radiation 591) operating in the blue spectral region. For fluorene and trans-stilbene we used a frequency doubled modified ring dye laser (Spectra Physics 380D). The doubling crystal, made of $LiIO_3$, was placed intracavity and angle tuned [4]. Both lasers operated single frequency with a bandwidth below 3 MHz. For relative frequency measurements temperature stabilized, sealed-off Fabry-Perot interferometers were used with accurately gauged free spectral ranges. The absolute frequency calibration in the UV is most easily performed by the fundamental wavelength of the dye laser. During a scan a small fraction of the fundamental laser power is used to measure the absorption spectrum in an iodine cell as a reference [5]. For the measurements on T we employed a home-built wavelength meter of the Michelson interferometer type [3]. This apparatus compares the laser wavelength with the accurately known wavelength of a stabilized He-Ne laser.

3. RESULTS AND DISCUSSION

3.1. Fluorene

We studied [6] the $S_1(^1B_2) \leftarrow S_0(^1A_1)$ transition in F and the related transition in the F-Ar VdW complex under rotational resolution. The 0^0_0 band in F exhibits a strong spectrum around 296 nm. The observed linewidth amounted to 15 MHz, due to the residual Doppler width in our spectrometer. Even most of the Q-branch transitions were resolved. The band consists of an a-type transition, corresponding to a transition dipole moment along the long molecular axis. A total of 225 lines in a central region of 20 GHz were assigned and fitted to an asymmetric rotor model. The fit proved excellent, with a standard deviation of 7.5 MHz. The rotationless transition frequency ν_0 was obtained and the rotational constants both in ground and excited state (table 2). All

TABLE 1 Rotation free transition frequencies (ν_0) and relative shifts ($\Delta\nu=\nu-\nu_0$) for fluorene (F), tetracene (T), trans-stilbene (tS) and their Van der Waals complexes.

	ν_0 (cm^{-1})	$\Delta\nu_0$ (cm^{-1})
F (0-0)	33 775.547(5)	
F-Ar	33 731.595(5)	-43.952(3)
T (0-0)	22 396.53(2)	
T-Ar		-41.67(5)
T-Kr		-66.9(1)
T-Xe		-110.0(1)
$T-Ar_2$		-80.6(1)
$T-Kr_2$		-124(1)
T (311 cm^{-1})	22 707.84(2)	
T-Ar		-41.42(5)
T-Kr		-66.5(1)
$T-Ar_2$		-79.9(1)
$T-Kr_2$		-123.4(1)
T (471 cm^{-1})	22 867.62(2)	
T-Ar		-41.52(5)
T-Kr		-66.9(1)
$T-Ar_2$		-80.0(1)
tS (0-0)	32 234.05(5)	
tS-Ar		-40.03(5)
tS-Ar		-63.04(5)

TABLE 2 Rotational constants (MHz) of fluorene, the fluorene-argon complex and tetracene in the ground state S_0 and the first excited electronic state S_1 ($\Delta A=A'-A''$, etc.)

		fluorene	fluorene-argon	tetracene
S_0	A''	2 183.2(33)	811.1(29)	1 630(1)
	B''	586.520(69)	468.58(14)	213.4(2)
	C''	463.239(65)	401.58(13)	188.8(2)
S_1	ΔA	-73.387(14)	-1.402(27)	17.4(12)
	ΔB	6.716(38)	1.437(31)	-1.81(8)
	ΔC	0.734(41)	4.961(26)	-1.19(8)

lines, even the weak ones, could be accounted for. From a fit of the line intensities with the rotational temperature as adjustable parameter we obtained a temperature T_{rot}=2.3(3) K for the molecules in the beam.

The observed transition, shifted $-44\ cm^{-1}$ (table 1) with respect to the F 0_0^0 band was assigned to the F-Ar VdW complex (figure 2). Since this complex has smaller rotational constants than the parent molecule, its spectrum is more dense. Nevertheless the P and R branch are still well resolved. The linewidth was again 15 MHz. In the central 23 GHz region of the band we assigned 150 lines. A fit to the asymmetric rotor Hamiltonian yielded ν_0 and the rotational constants as given in table 2. Again the fit proved to be very satisfactory, with a 7.6 MHz standard deviation. Analysis of the spectral intensities showed a single Boltzmann distribution with a rotational temperature of T_{rot}=2.1(4) K. Within experimental accuracy the rotational temperatures of the parent molecule and the complex are thus the same.

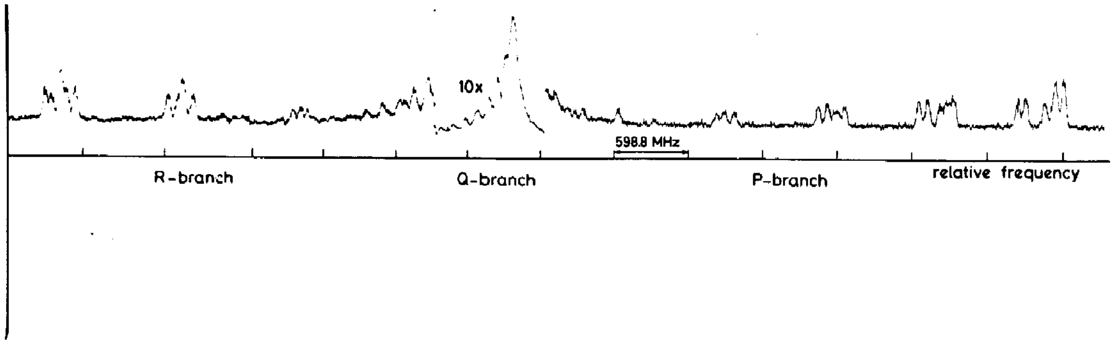

Figure 2. Part of the fluorene-argon rotational spectrum around 33 731.595(5) cm^{-1}. The frequency markers are spaced 598.64 MHz.

The position of the argon in the complex can be determined [6] from a comparison of the moments of inertia along the principal axis of the parent molecule and the complex. It follows that the argon is located in the bisecting plane of the molecule at a distance from the center of mass of fluorene of r=(3.46±0.03) Å with $\theta=\pm(8.8\pm1.0)^\circ$, where θ is the angle with the z-axis. The ambiguous sign of θ arises from the fact that the moment of inertia tensor depends quadratic on the relative argon coordinates. This problem can be solved by studying the rovibronic spectrum of a deuterated F-Ar complex. Such a study is presently carried out.

We performed a model calculation of the F-Ar complex using a Lennard-Jones 6-12 potential with pairwise interactions. Three-body interactions were neglected. This method was described by Ondrechen et al. [7]. The calculated absolute minimum is above the center ring of the molecule at the argon coordinates $(x_0,y_0,z_0)=(0.13,0,3.48)$ Å, with respect to the center-of-mass coordinate system of F. Figure 3 shows two cuts through the coordinates of the potential minimum. The experimentally determined positions are very near this minimum.

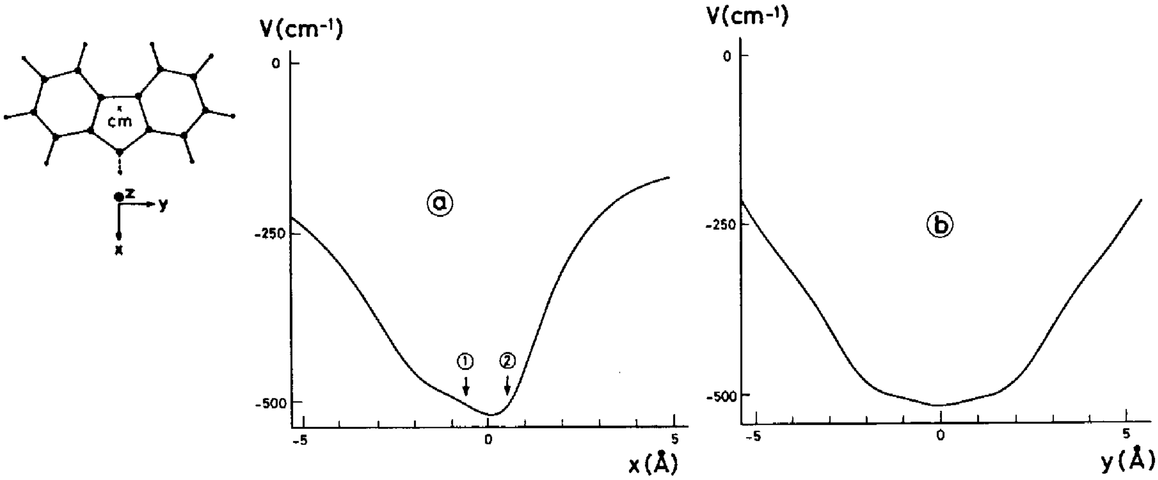

Figure 3. Rotational energy curves for a single argon with fluorene. The position of the argon is given in the center-of-mass coordinate system of fluorene. (a) Minimal potential energy as a function of x (y=0 and z is adjusted); the two possible experimental positions are indicated. (b) Energy as a function of y (x=0.13, z=3.48).

3.2. Tetracene

We obtained fluorescence excitation spectra of the $S_1(^1B_{2u}) \leftarrow S_0(^1A_g)$ electronic transition of tetracene [8,9]. The rotational band of the 0-0 vibrationless transition was resolved as well as vibronic bands belonging to the 311 cm^{-1} and 471 cm^{-1} vibrational modes in the excited S_1 state. The spectra of the 0-0 and 311 cm^{-1} bands are almost identical. They were both assigned as a b-type transition, corresponding with a transition dipole moment along the short molecular axis. The spectra consist of hundreds of strong spectral lines, spreading over a wide range. The 471 cm^{-1} band is connected to a not totally symmetric vibrational mode. The transition to this mode is symmetry forbidden but becomes weakly allowed by a coupling with the $S_2(^1B_{1u})$ state. The band becomes long axis polarized and shows an a-type structure. A total of 65 lines was assigned in the central part of the b-type perpendicular transitions and 160 lines in the a-type parallel band. A fit to the asymmetric rotor model was excellent. The obtained rotational constants for the different transitions did not differ within their statistical undertainty. The values given in table 2 stem from combined data of the various bands. To our knowledge T is the largest molecule reported so far with a fully resolved and assigned rotational spectrum. From the intensity distribution in the 471 cm^{-1} band, where a number of single lines were observed, we determined the rotational temperature in the molecular beam. A single Boltzmann distribution was found with T_{rot}= 2.3(3) K. All strong spectral features in the different bands could be accounted for. The linewidth in the spectra is 15 MHz, and is determined by the residual Doppler width of the spectrometer.

The assignment of transitions in tetracene-noble gas VdW complexes has been reported by Amirav et al. [10,11]. The complexes have transitions, more or less regularly red shifted with respect to the related transition in the parent molecule. We explored VdW molecules containing argon, krypton and xenon. These are readily formed in the molecular beam by using the noble gas as seeding gas. We performed model calculations of the T-R (R=Ar,Kr,Xe) complex, using a Lennard-Jones potential [7]. The distance between the R-atom and T was adjusted for minimum

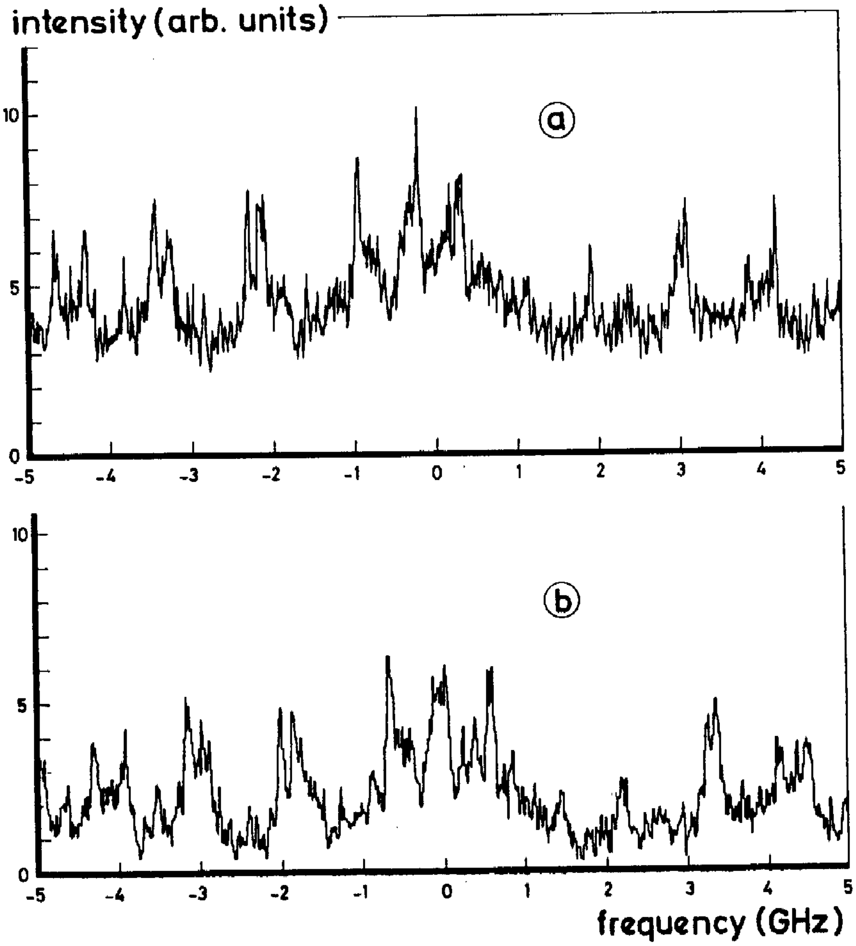

Figure 4. Rotationally resolved spectra of tetracene-argon. (a) The 311 cm^{-1} band; (b) the 0_0^0 transition.

energy. The absolute minima are found above the inner rings of T. The potential depicts a double well structure along the long molecular axis. Consequently a tunneling motion may exist of the R atom along the molecular plane, resulting in doubling of the rotational bands. The potential barrier is most pronounced for argon and very shallow for the other considered noble gases. Other potential minima were shown to be absent and the existence of chemical isomers of the complex is thus unlikely. A study of the rotational spectra provides a test of the calculated potential surface.

High resolution excitation spectra were observed of T-R (R=Ar,Kr, Xe) complexes. In figure 4 and 5 rotationally resolved spectra are shown of T-Ar and T-Kr. The 0-0 band of T-Xe is not indicated. It consists of some small humps on a broad background. Other bands of T-Xe are of very low intensity. The red shifts of the complexes (table 1) differs for argon, krypton and xenon, but is almost constant for different bands in a complex. This strongly supports the indentification. The 0_0^0 and 311 cm^{-1} band in T are identical. In T-Ar they still look much alike (figure 4) with a clear perpendicular structure. In T-Kr these bands, however, are quite different, with an almost unrecognizable structure (figure 5). The 471 cm^{-1} band in T-Ar is of parallel shape like it is in the parent molecule. The orientation of the a-axis in both molecules is thus very much alike. The weak 471 cm^{-1} band in T-Kr has no recognizable pattern. It contains a small hump on a broad structureless background. The linewidth in the T-Ar spectra is estimated at 15 MHz and limited by our spectrometer. For T-Kr and T-Xe complexes the fluorescent lifetime has diminished to 11 ns and 1.5 ns respectively [12] and no individual lines were observed. It is clear that the T-Kr and T-Xe spectra show no ordinary rotational shape but are heavily perturbed. This anomalous structure is too pronounced to be caused by the different isotopes of krypton or xenon. For T-Ar perturbations are not so clear. However, despite much effort we could not assign the spectra. There seems to be an excess of lines in the parallel band, while the sequence of Q-branches in the perpendicular band looks distorted. All bands are observed as single transitions. We did not find evidence for a splitting due to a tunneling type motion of the inert gas atom. Such splitting either does not exist or it is very small. Also spectra of the T-Ar_2 and T-Kr_2 complexes have been observed. The red shift of a T-R_2 complex with respect to T is not twice the shift of a T-R molecule (table 1). The transitions in the T-R_2 complex qualitatively behave in the same way. They show hardly any structure and consist of a broad flat band. No individual lines were observed.

We conclude that the perturbations in the complexes increase with excited state energy, with the number and with the mass of the attached noble gas atom. The effects may be caused by S-T intersystem crossing, S_1-S_0 state mixing or even with a coupling of the S_1 state with higher energy levels. The latter interaction is present in the T molecule as the 471 cm^{-1} vibrational band gains its intensity by a coupling of the S_2 state.

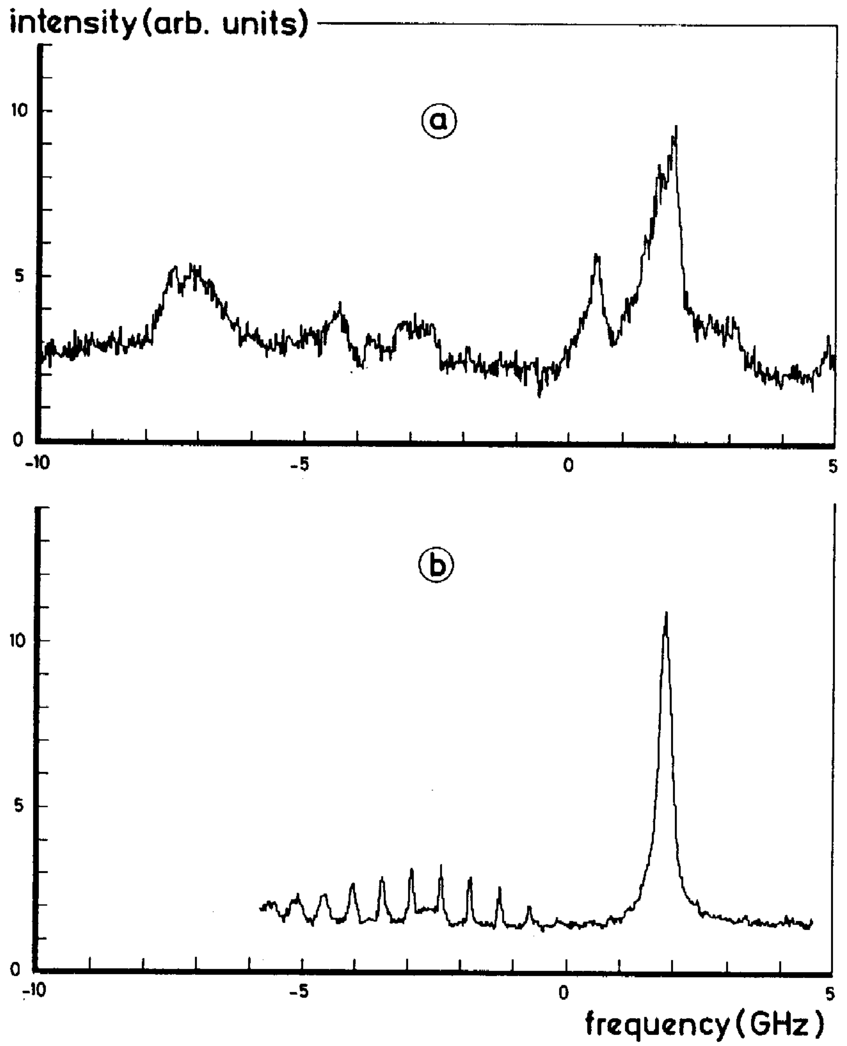

Figure 5. Comparison between the 311 cm^{-1} (a) and 0_0^0 (b) rovibronic spectra of tetracene-krypton.

3.3. Trans-stilbene

The geometry and photo-isomerization of stilbene (diphenylethylene) forms an intriguing problem in physical chemistry. The energy of the electronic states strongly depends on the angle θ of rotation about the ethylenic bond. The first excited S_1 electronic state with minima at the trans ($\theta=0°$) and cis ($\theta=180°$) configuration is crossed by the S_2 state, which has an absolute minimum at the perpendicular ($\theta=90°$) geometry. In the S_0 ground state the trans and cis configuration are separated by a large energy barrier and a perpendicular configuration does not exist. It was shown [13] that the S_0 ground state of tS has phenyl groups rotated by about 30° with respect to the ethylene plane and is thus non-planar.

An experimental assignment of the vibrational modes in the S_0 and S_1 states was presented by Syage et al. [14] and by Zwier et al. [15]. The fluorescent lifetimes [16] strongly decrease at excited state vibrational energies above 1200 cm^{-1}. We measured high resolution fluorescence spectra of tS and the tS-Ar VdW complex to obtain more detailed information on the geometry and internal motion of both molecules. A total of 8 vibronic transitions in tS has been studied under rotational resolution in a molecular beam experiment. The excited state vibrational energy ranges up to 1447 cm^{-1}. The tS 0-0 vibrationless band is depicted in figure 6. It appeared that the observed linewidth in all considered bands of tS exceeded the instrumental linewidth and amounted about 80 MHz in the lower vibrational states. These observed widths conform with lifetime measurements [16]. At higher energies (i.e. above 1200 cm^{-1}) the spectra become congested, probably due to an increased linewidth. The bands considered all show very similar spectra with only detailed differences.

One can estimate the moments of inertia and consequently the rotational constants of tS from the theoretical geometry. The molecule with phenyl groups rotated by about 30° forms an almost prolate symmetric top. However, the observed spectrum of for example the 0-0 band (figure 6) does not resemble a symmetric top transition. The experimental density of lines is higher than expected. Although assignment of the spectrum

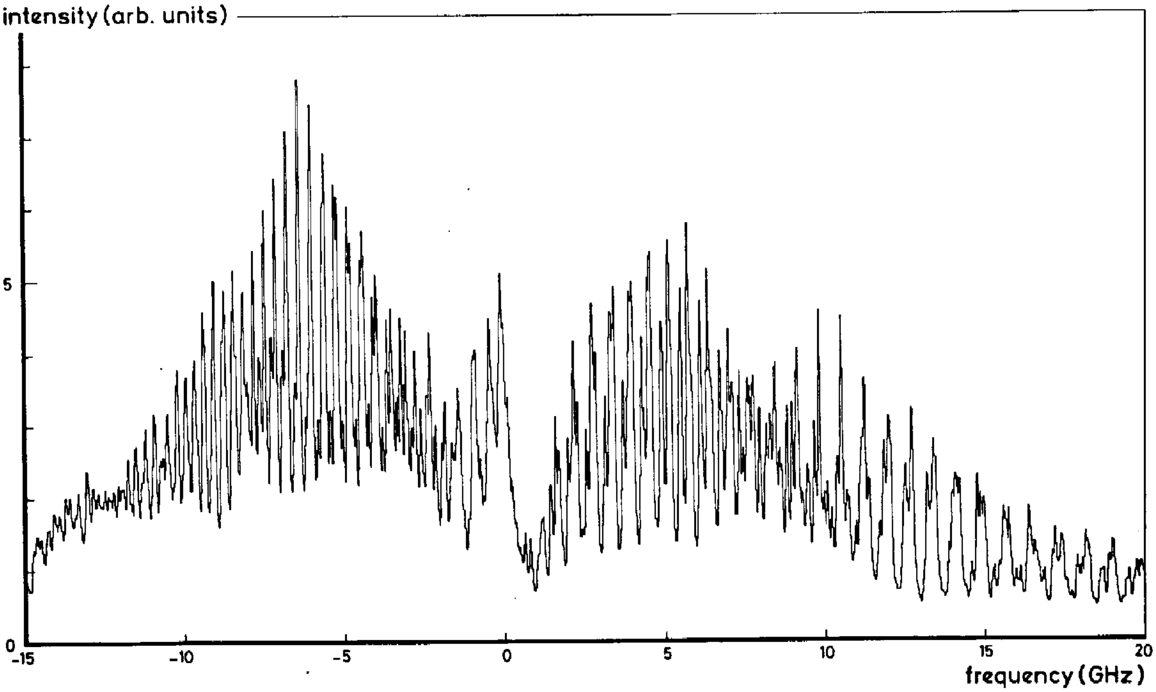

Figure 6. Fluorescence excitation spectrum of trans-stilbene 0_0^0, around 32 234.05 cm^{-1}.

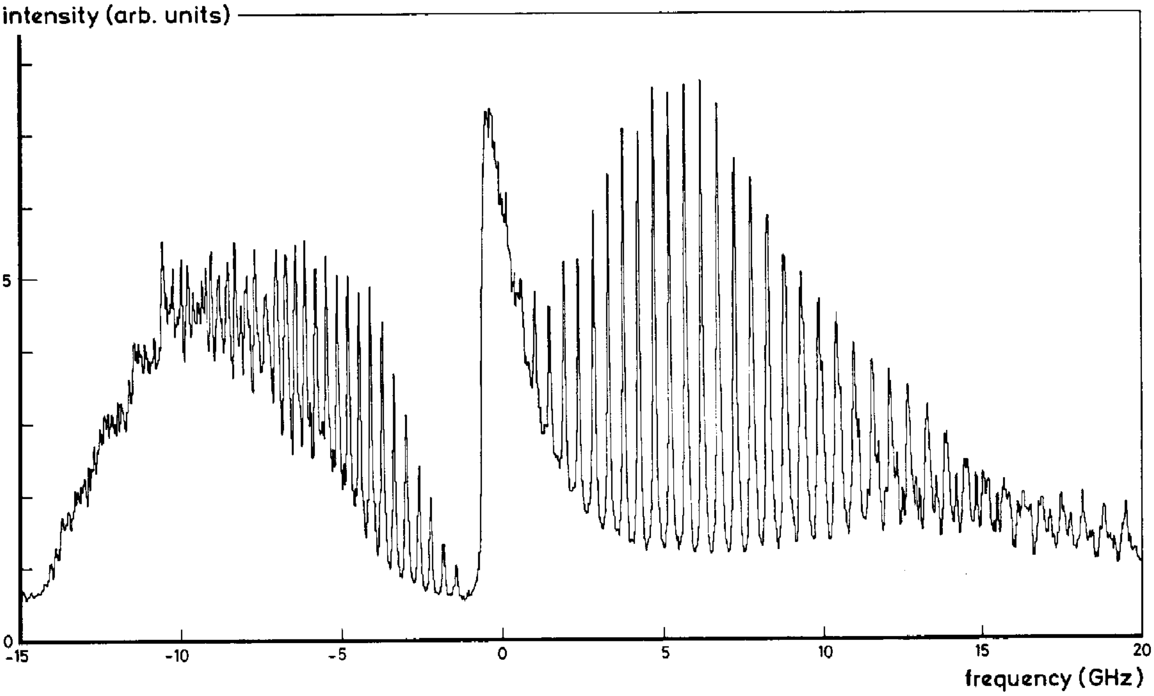

Figure 7. Fluorescence excitation spectrum of trans-stilbene-argon. The band is shifted -63.04(5) cm^{-1} with respect to stilbene 0_0^0.

has not yet been accomplished, we tend to the conclusion that the tS spectra show evidence of an internal motion of the phenyl groups. Such an internal motion would increase the number of observed spectral lines. The process of trans-perpendicular-cis isomerization is too slow to be observed in these fluorescence excitation spectra.

VdW complexes of tS with noble gas atoms form a very interesting subject, Not only the determination of the complex structure is of interest but it is also clear that an attached atom will hinder isomerization. The internal motion will also be affected. Bands of VdW complexes of tS containing helium and argon have been observed at vibrational resolution [15,17]. Unfortunately the intensity of the bands is low and an unambiguous assignment could not be made. Complexes with helium show regularly shifted bands with respect to the related 0-0 transition in the parent molecule. Complexes with argon, however, are much more irregularly shifted.

We observed two bands of complexes of tS with argon, shifted (table 1) -40 and -63 cm^{-1} with respect to the 0_0^0 band if tS. The -63 cm^{-1} band is depicted in figure 7. The linewidth in both spectra did not deviate from the linewidth observed in the parent molecule. On first sight, the spectrum of figure 7 resembles a near symmetric top band. The -40 cm^{-1} transition shows a somewhat less regular structure but has a comparable spacing of lines. It is remarkable that these bands have a less dense spectrum compared to tS, although the rotational constants are expected to be smaller. This strongly suggests that the internal motion of the phenyl groups is diminished in the complex. We have not yet completed the assignment of these rotationally resolved spectra. However, we come to the preliminary conclusion that the derived rotational constants of both bands compare very well with a complex geometry of a single argon atom placed above a phenyl group of the parent molecule. Other configurations or complexes with more argon atoms have rotational constants, which deviate too much from the experimental values.

4. ACKNOWLEDGEMENTS

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