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**Near UV High Resolution Molecular Spectroscopy the  
Rovibronic Spectra of Large Organic Molecules and Their  
van der Waals Complexes**

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Molecular spectroscopy is still one of the main sources of information about vibrational, electronic and rotational states in molecules. High resolution is needed to resolve rotational structure in large molecules (of tens of atoms) and small effects due to, for example, singlet-triplet interaction as recently observed in pyrazine [1]. We have achieved the required high resolution in optical spectra by combining a single-frequency dye laser with a well collimated molecular beam. As of the methods to reduce (or eliminate) the linewidth due to Doppler broadening, the application of a molecular beam is one of the most straightforward and simplest. It has the additional possibility to reduce the internal vibrational and rotational temperatures of the molecules by using the seeded beam technique. This not only simplifies the spectra considerably, but also allows the formation of complexes in the ultra cold beam. Since most molecules have their lowest lying electronic transitions in the UV region a reliable easy tunable single-frequency source of radiation is the crucial point in high resolution molecular spectroscopy.

A novel method of second harmonic generation (SHG) in a single-frequency dye laser has been developed [2]. A tuning range between 293 and 330 nm assures matching of the frequency of the radiation field with electronic transitions in many organic and anorganic molecules. The SHG is obtained by placing a single  $\text{LiIO}_3$  angle-tuned crystal of 1 mm thickness in a modified Spectra-Physics ring dye laser. The doubling method based on the fact that phase matching in a  $\text{LiIO}_3$  crystal can be achieved by changing one angle only ( $\theta$ ) independent of the second angle ( $\varphi$ ) like KDP and its analogues. Furthermore,  $\text{LiIO}_3$  is less hygroscopic and insensitive for thermal detuning by residual absorption in the crystal. In practice, the phase-matching condition is fulfilled by a variation of two mechanical degrees of freedom of the Brewster-positioned crystal. The first is a rotation around the normal to the crystal and the second is a slight change of the direction of the fundamental radiation around the Brewster angle. By this method phase matching was achieved without disturbance of the linear polarization of the intracavity fundamental wave. CW powers up to a few milliwatts allowed the recording of spectra with high signal-to-noise ratio. Stabilized scans up to 150 GHz with a 500 kHz (UV) linewidth (linewidth-to-scan ratio  $10^6$ ) were routinely obtained. The ratio of the total tuning range to the linewidth is  $2 \times 10^8$ . The frequency has been monitored by a temperature-stabilized Fabry-Perot etalon and the iodine absorption spectrum at the fundamental laser frequency.

The molecular beams were formed by expanding noble gases (He and Ar) through a nozzle with a small admixture of the molecules to be studied. The nozzle diameter and

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the total backing pressures were typical 80  $\mu\text{m}$  and 7 bars, respectively. The temperature of the source varied between 100 and 200  $^{\circ}\text{C}$  in the presently reported experiments. The source, however, could be heated as high as 550  $^{\circ}\text{C}$ . To facilitate preliminary easy searching for transitions a low resolution set-up has been used. In this arrangement the laser beam crossed the "free jet" molecular beam up to a few millimeters downstream from the nozzle. Strong vibrationally well resolved spectra could be obtained. Since the residual Doppler linewidth amounted up to 600 MHz, rotational spectra of large molecules are hardly resolved. In order to achieve rotational resolution the molecular beam was strongly collimated by two diaphragms with a two-step differential pumping system. The laser radiation crossed the molecular beam 30 cm from the source, thus reducing the residual Doppler width to 35 MHz. The results discussed below were all obtained with the high resolution set-up.

The spectra have been obtained by fluorescence excitation. The collected undispersed fluorescence has been measured by a standard photon counting system. Naphtalene, perdeuterated naphtalene and fluorene have been chosen as test molecules. A typical vibronic band extended over 120 GHz and consisted of a few hundred well resolved rotational lines. The relative line intensity measurements have been used to determine the rotational temperature. For all species studied this temperature was about 2 K. Effects of the nuclear spin statistics on the line intensities have been observed and checked.

The  ${}^1\text{B}_{3\text{U}} \leftarrow {}^1\text{A}_\text{g}$  electronic transitions in naphtalene and perdeuterated naphtalene have been studied [3]. For both isotopic species two vibronic bands, the  $0_0^0$  a-type transition at the electronic origin and the much stronger  $8_0^1$  b-type transition have been observed. The central frequencies and rotational constants for ground and excited states have been determined from a rotational analysis of the spectra. From the inertia defect it has been concluded that the naphtalene molecular is planar in both ground and excited electronic state.

In cold supersonic molecular beams complex formation between the atoms and molecules in the beam is easily achieved. As an example we studied the argon-fluorene van der Waals complex. The  ${}^1\text{B}_2 \leftarrow {}^1\text{A}_1$  electronic transition of the bare fluorene molecule showed a very strong well resolved rotational spectrum centered around the band origin  $\nu_0 = 33775.547$  (5)  $\text{cm}^{-1}$ . From the rotational analysis it has been concluded that the skeleton of the molecule (see fig. 2) is planar [4]. Shifted 43.952 (2)  $\text{cm}^{-1}$  to the red a spectrum has been observed, which was identified as that of the Ar-fluorene complex. The transition was about a factor 100 weaker than that of the bare fluorene molecule. The central 9 GHz of the Ar-fluorene spectrum is shown in fig. 1.

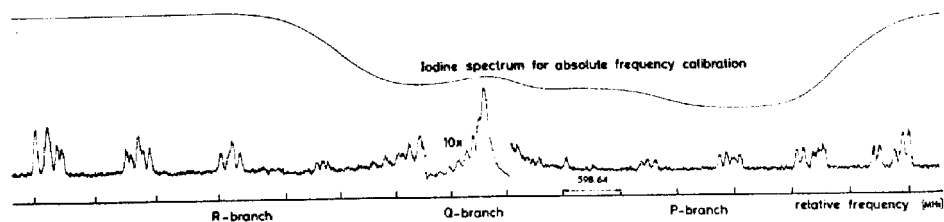


Fig. 1.: Spectrum of the argon-fluorene van der Waals complex. The lower frequency markers are at every 598.64 GHz

From the change between the moments of inertia of fluorene and Ar-fluorene the structure of the complex has been deduced. The structural parameters depicted in Fig. 2 are  $\vartheta = \pm (7.8 \pm 1.5)^\circ$  and  $z_0 = (3.44 \pm 0.03)\text{\AA}$ . The uncertainties reflect the effects of the large amplitude motion of the Ar atom in the complex. Within the experimental uncertainty the structure of the complex is unaltered in the excited electronic state. We were not able to observe rotationally resolved spectra of the Ar<sub>2</sub>-fluorene cluster. The reason for this has been attributed to a fast dissociation of the Ar<sub>2</sub>-fluorene complex after electronic excitation.

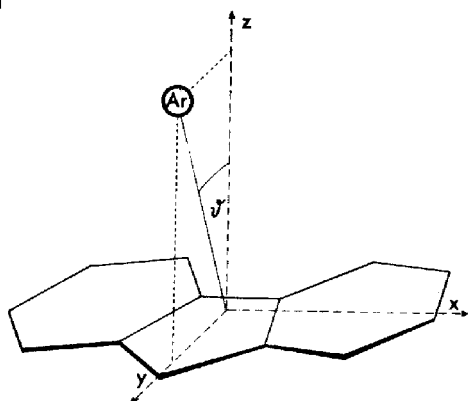


Fig. 2.: Structure of the Ar-fluorene complex. The origin of the coordinate system has been chosen at the centre of mass of the fluorene

The relative inaccuracies in the determination of the rotational constants in the present work were  $10^{-3}$ , mainly limited by the thermal stability of our marking Fabry-Perot interferometer. The uncertainties can greatly be reduced up to  $10^{-6}$  by locking the interferometer to a Doppler-free transition in iodine.

The very high resolution, strong signals and complexity of the rovibronic bands result in spectra with information capacity of the order of several megabits. In the present experiments the rise time of a standard pen recorder significantly limited the scanning speed of the laser. The application of fast data acquisition electronics and extension of the tunability of the existing UV single-frequency radiation sources will greatly enlarge the versatility of high resolution spectroscopy and open a new dimension for the study of large molecules.

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