Structure of the Benzene-Argon Complex in the Gas Phase at 3 Kelvin

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The structure of the benzene-argon complex is determined from a high resolution band contour of the ν_6 transition of the complex measured in a hypersonic jet. It is shown that the argon is located on the main symmetry axis of the benzene molecule. The distance from the center of the benzene ring is found to be 3.4 Å.

New spectroscopic data of large molecules can be obtained when one expands the molecules in a seeded hypersonic jet [1]. The efficient cooling of the rotational temperature to a few Kelvin eliminates the spectral congestion at room temperature and allows for separation of vibrational bands. In addition, when one excites the molecules with a high resolution laser single rotational state analysis can be performed [2], which is not possible at room temperature.

It is known that molecules when expanded in a seeded beam readily form complexes with the carrier gas. The hypersonic jet thus permits a study of formation, structure and kinetic behaviour of a complex with a single bound noble gas atom as well as a molecule with many inert atoms, a matrix like environment and all stages between these two "phases". The formation of these Van der Waals complexes has been deduced from fluorescence excitation spectra where the stoichiometry of the complexes is obtained from the shift of the complex peaks relative to the bare molecule peak, using simple sum rules or the effect of the pressure of the carrier gas on the relative intensities of the peaks [3]. A method for the direct analysis of such complexes is the resonant two color photoionization together with time-of-flight mass analysis [4]. This gives a direct mass identification of each aggregate, however it provides no information on the structure of such complexes. This further information can be obtained from the rotational analysis of the complex band contour either in ionization or fluorescence studies. Here we show the results for the benzene-argon complex in a hypersonic jet. The structure is derived from the comparison of the observed fluorescence excitation spectrum with a symmetric rotor calculation. The supersonic apparatus used here has been described elsewhere [5]. The benzene pressure was held at 21 Torr in front of the nozzle and a carrier pressure of 2 atm argon was used. Under these conditions one achieves a final rotational temperature of 3 Kelvin. The benzene-argon complex is excited with the frequency doubled output of a dye laser (Coumarin 500) and the fluorescence is detected perpendicular to the laser and the hypersonic jet. The frequency tuning of the dye laser is achieved with a pressure tuned intracavity etalon which provides resolution of 0.15 cm^{-1} in the UV.

Figure 1 shows the fluorescence excitation spectrum of the benzene-argon complex with the excitation of the ν_6 band of the benzene in the complex. This experimental curve is now fitted to a computed absorption spectrum. From the shape of the envelope it is immediately apparent that this is a perpendicular band and that the argon cannot lie in the plane defined by the benzene ring. We then assumed that the argon is positioned on the main symmetry axis of the benzene molecule. If one in addition assumes a weak Van der Waals interaction, the electronic structure of the benzene should not be seriously affected by the complexation and therefore one can use the geometry of the bare benzene molecule to define the positions of the carbon and hydrogen atoms. These data can be obtained from the known spectroscopic data of the benzene absorption spectra [6]. Now the rotational constants for the complex for different positions of the argon are computed and the values are used as

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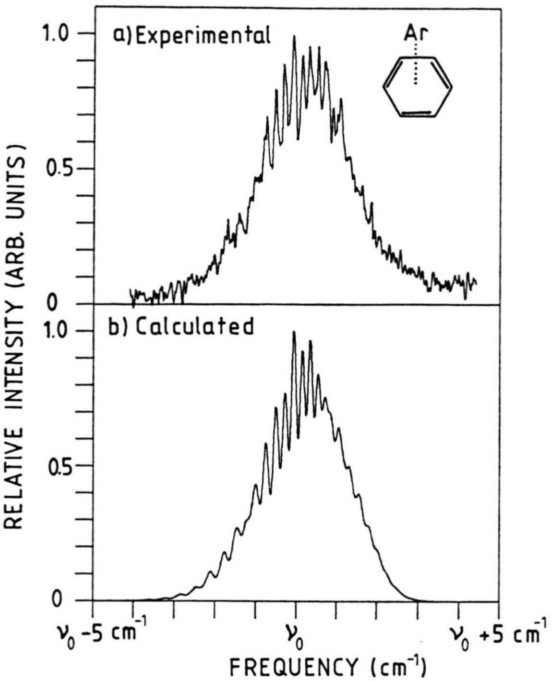

Fig. 1. Benzene-argon complex spectrum in a hypersonic jet. a) Fluorescence excitation spectrum $\nu_0 = 38588.4\ \mathrm{cm}^{-1}$. b) Calculated absorption spectrum.

Table 1. Rotational constants for the benzene-argon complex.

Rotational Constant	A (cm^{-1})	$B = C$ (cm^{-1})
Ground state	0.0945	0.0427
Excited state	0.0898	0.0424

Coriolis constant -0.6 [6].
Argon distance above benzene ring 3.4 ± 0.2 Å.

input for the contour analysis. The ν_6 vibration of benzene has e_{2g} symmetry and is two-fold degenerate. The coriolis coupling constant of -0.6 of the bare benzene molecule [6] is also used for the complex. The temperature of 3 Kelvin for the simulation was taken from the bare benzene molecule spectrum with well defined rotational constants measured under identical experimental conditions. In the complex the symmetry also is changed from D_{6h} of benzene to C_{6v}. The different statistical weights in this case are also included in the simulation. For a laser bandwidth of $0.15\ \mathrm{cm}^{-1}$ in the calculation a best fit was obtained for a distance of 3.4 Å of the argon from the center of the benzene ring. The calculated absorption spectrum is shown in figure 1 b and the rotational constants are given in Table 1.

The comparison between the experimental curve and the computed spectrum now reveals the structure of the complex and confirms that the argon is located on the symmetry axis. It also can be shown that the distance from the center of the benzene ring is the same for the ground and excited state of the complex within the estimated error of 0.2 Å of the position of the argon. The distance of the argon is within the range of theoretical expectations [7] and slightly larger than in the case of benzene-helium [8], but much larger than for the argon-HF complex where a distance of 2.63 Å is found between the argon and the Hydrogen [9].

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