Ion Dip Spectrum of the Fluorobenzene-Argon van der Waals Complex in a Supersonic Jet

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The ion dip spectrum of the fluorobenzene-Argon van der Waals complex has been measured and the complex shift in the ground state is determined. The observed dips then could be assigned by comparison with the ion dip spectra and hotband spectra of the fluorobenzene molecule.

Introduction

For the last years an increasing interest in van der Waals clusters as a source of information about weakly bound systems can be observed. This has led to a great number of investigations, but nearly exclusively for electronically excited clusters or cluster ions. The electronic ground state is even more interesting, but experimentally only few methods are applicable, like IR spectroscopy and CARS. For cluster measurements only double resonance techniques are suitable, because in supersonic jets many different complexes are formed simultaneously and therefore the identification of the spectra is a great problem for conventional spectroscopy. These double resonance spectra therefore have to be coupled with mass spectroscopy to identify the different species. A suitable technique here is 'stimulated emission pumping' (SEP), which is used in 'fluorescence dip spectroscopy' and in 'ion dip spectroscopy'. These methods use a first laser pulse for resonant excitation of the interesting molecule to an upper electronic state (pumping) and then probe the population of this state by measuring the total fluorescence or the multiphoton ionization signal from there. With a second tuned laser at a different frequency transitions to vibrational states in the electronic ground state can be induced. These transitions depopulate the excited state and a decrease in fluorescence or MPI signal can be observed. In the case of molecular complexes the ion dip spectroscopy can be coupled with mass detection which in addition allows disentangling the spectra which arise from different sized complexes which are formed simultaneously in the jet. Dai et al. [1] have measured fluorescence dips of the glyoxal-argon complex and Stanley et al. ion dips for the phenylacetylene-NH_3 complex [2]. We can report ion dips of the fluorobenzene-argon complex which can be used as a prototype system for the weak interaction between a noble gas atom and an aromatic ring system.

Experimental

Figure 1 shows a schematic diagram of the experimental setup used in this experiment. The third harmonic of a Nd: YAG-Laser (Quanta Ray DCR-1A) is used for pumping two dye lasers (Quanta Ray PDL-1). With the second harmonic of the first dye laser (Coumarin 153) the excitation of the fluorobenzene argon complex to the resonant intermediate S_1 state is performed. The frequency doubled light of the second, tuned dye laser (Coumarin 153) was used for ionization of the complex and simultaneously dumping to the electronic ground state. The bandwidth of both lasers was 0.3 cm^{-1} in the UV. Both laser intensities were measured with photodiodes for normalization of the spectra. The jet apparatus consists of a nozzle chamber and a main chamber to which a reflectron time-of-flight mass spectrometer is attached. The supersonic jet is produced by seeding fluorobenzene at 273 K in Argon with a backing pressure of 5 bar and expanding the mixture through a pulsed nozzle with a 0.2 mm diameter orifice. The jet is skimmed 3 cm downstream the jet by a skimmer with a 1 mm opening. The two laser beams enter the main chamber coaxially from opposite directions. Two 220 mm focal length lenses are used to combine the two laser beams in a common focus on the center of the supersonic beam. The ions produced are extracted with a two

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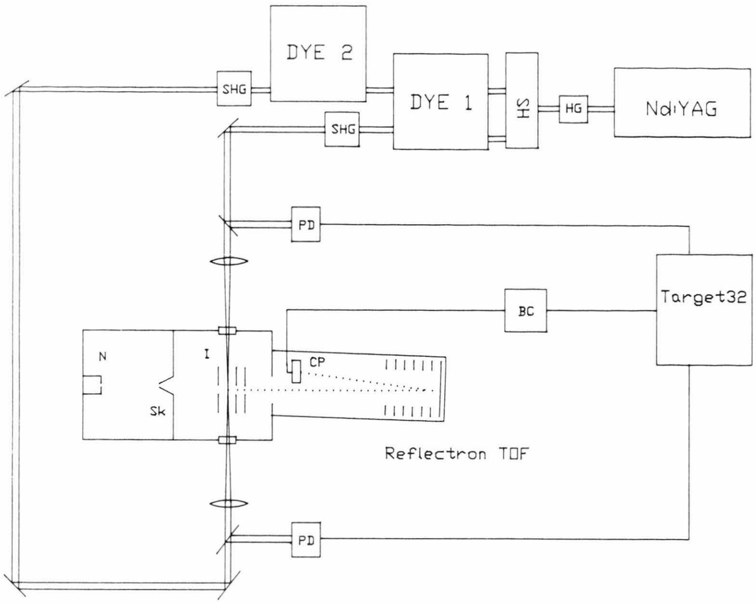

Fig. 1. Setup for the ion dip experiment: The frequency doubled output of two dye lasers is used for ionizing the complexes in the supersonic jet, which are mass resolved with a reflectron time of flight mass spectrometer. Data aquisition and experiment control is performed by a laboratory computer. HG = harmonic generator, HS = harmonic separator, SHG = second harmonic generator, PD = photodiode, BC = boxcar integrator, Target 32 = laboratory computer, N = nozzle, Sk = skimmer, I = ion optics, CP = channel plate detector.

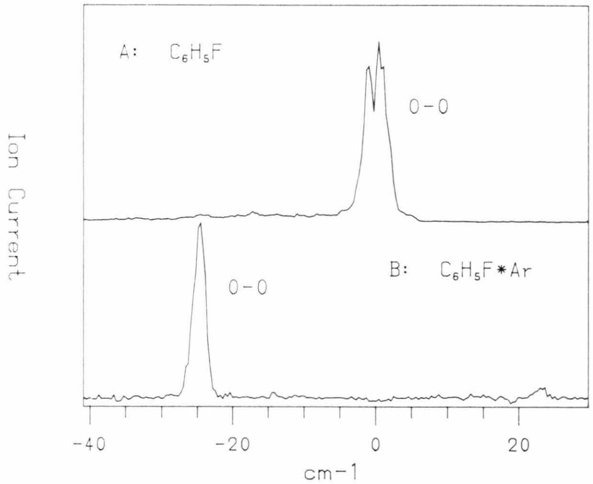

Fig. 2. Ion current spectra of fluorobenzene and fluorobenzene-Ar: Resonant excitation of C_6H_5F with partially resolved rotational structure (A). The $C_6H_5F * Ar$ spectrum (B) is red shifted by 23 cm^{-1}. Excitation is to the vibrationless S_1-state of the fluorobenzene in both cases.

stage ion optic into the reflectron time of flight mass spectrometer. The total drift length is 1.5 m and a resolution of $m/\Delta m$ of 2000 is achieved. The ion signal is integrated by a boxcar integrator (Stanford Research).

Experiment control and recording of the integrated ion signal and the laser intensities is performed by a laboratory computer (FORCE Target 32).

Results

To obtain the ion dip spectra the first laser has to be tuned to a resonant intermediate state of the complex. For this we choose the vibrationsless S_1 state of the fluorobenzene molecule. Figure 2 now shows the ion current excitation spectra of the bare fluorobenzene molecule and the fluorobenzene-Argon complex in the vicinity of the $S_1 \leftarrow S_0$ transition. At the origin the bare fluorobenzene molecule shows a double peak with a shoulder on the blue side which is due to a partially resolved rotational band at 37816 cm^{-1} (Figure 2A). The corresponding 0–0 transition of the fluorobenzene-Argon complex is red-shifted by 23 cm^{-1} and shows only one single peak (Figure 2 B), a behavior which was also found for the ν_6 transition of the benzene-Argon complex [3].

Now the first laser is tuned to a fixed frequency near the center of the rotational band of either the fluorobenzene or the fluorobenzene-Argon complex, and the second laser is scanned. The frequency of this laser is tuned in the range from 36949 cm^{-1} to 37019 cm^{-1}. With this laser the resonant excited species is ionized and the ion current due to the second laser is observed (Figure 3A). When one excites the fluorobenzene-Argon complex one now finds dips in the ion current spectra whenever the laser frequency coincides with a $S_0 \leftarrow S_1$ transition, and hence the intermediate state is also depopulated by stimulated emission to a vibrational level in the ground state. We

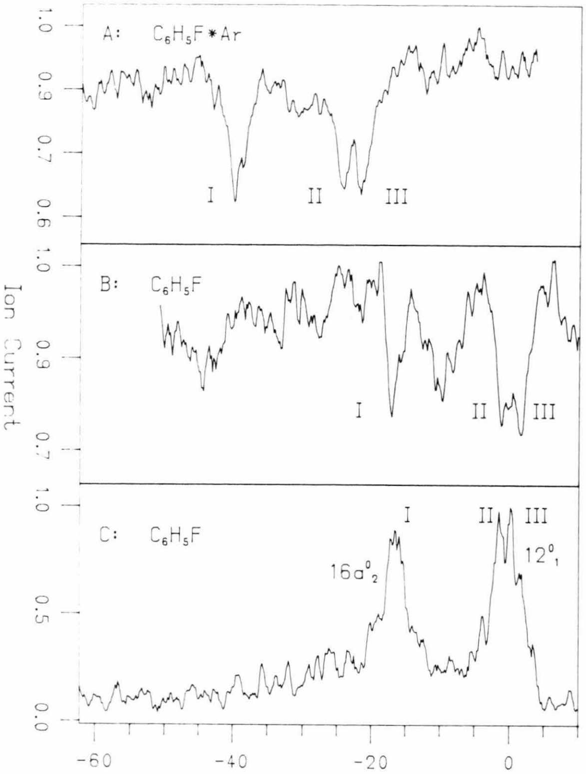

Fig. 3. Hot band spectrum of fluorobenzene and ion dip spectra of fluorobenzene and fluorobenzene-Ar: Curve A shows the spectrum of fluorobenzene-Ar when exciting the S_1 0–0 transition and dumping to $2\,\nu_{16a}$ (I) and ν_{12} (II, III). Curve B shows the ion dip spectrum of fluorobenzene when exciting the S_1 0–0 transition and dumping to $2\,\nu_{16a}$ (I) and ν_{12} (II, III). Curve C shows the corresponding hot band spectrum of fluorobenzene. The vibrational states $2\,\nu_{16a}$ and ν_{12} are still populated due to the inefficient cooling of vibrations in the jet.

now find two features in the spectrum, a single peak at 36 967 cm^{-1} and a double peak at 36 983 cm^{-1} and 36 986 cm^{-1}. To identify the vibrational states we also performed the experiment for the bare fluorobenzene molecule. A similar ion dip spectrum is observed which is blue shifted by 23 cm^{-1} (Fig. 3 B) compared to the complex. In addition to the peaks seen in the complex a third feature shows up between these complex related peaks. These dips in the molecule spectrum which now correspond to transitions to the vibrational excited ground state should also be observed in a corresponding hot band spectrum where those levels are thermally populated. In the supersonic expansion the cooling efficiency of vibrations in contrast to rotation and translation is inefficient and therefore even vibrational levels in the range of 800 cm^{-1} can still be populated. This now allows us to observe hot band spectra where the first laser is tuned and the second laser is held at a fixed frequency. Figure C now shows the hot band spectrum for the fluorobenzene molecule. The signal is very low but the main two features of the dip spectrum are easily reproduced. The center feature of the dip spectrum is not clearly observed and seems to be smeared out between the other peaks. This can be due to the fact that the dip spectra reflect the rotational transitions from a limited number of rotational states excited within the resonant peak, whereas the excitation spectra show broader bands with the complete ensemble of thermally populated rotational states [4]. It now was very interesting that we could not observe the corresponding hot bands in the complex spectrum whereas from the shape of the rotational bands a similar temperature of the complex compared to the bare molecule is expected.

Discussion

The hot band spectrum of the bare molecule can now be easily assigned from known room temperature spectra [5] and the peaks in the dip spectrum of the fluorobenzene correspond to the $16\,a^0_2$ (I) and 12^0_1 (II, III) transition. If one assumes only a minor effect of the van der Waals interaction on the intramolecular frequencies one expects the same shift of the vibrational bands as for the 0–0 transition. The peaks in the dip spectrum therefore can be assigned to the intramolecular transition within the fluorobenzene in the complex. The excess energy of the vibrational levels above the vibrationless ground state is 825.8 cm^{-1} for $2\,\nu_{16a}$ and 807.4 cm^{-1} and 810.0 cm^{-1} for ν_{12} where the double peak arises possibly from rotational splitting. The depth of the van der Waals potential now in the ground state is only in the order of 370 cm^{-1} for benzene-Argon [6] with a upper limit of 630 cm^{-1} [7] and 200 cm^{-1} for the p-difluorobenzene-Argon [8] and therefore vibrational predissociation of these states is expected. With our experimental setup the line width for the individual rotational lines in the dip bands cannot be resolved, but from the observed peaks the linewidth has to be lower than the laser bandwidth of 0.3 cm^{-1} which gives a lower limit for the lifetime of greater 0.1 ns for these levels. The absence of the hot band spectra in addition gives an upper limit of 100 µs due to the fact, that even if these 'hot' complexes would be formed in the expansion region, they would not survive longer than the flight time from the nozzle to the ionization region.

Conclusion

The ion dip spectroscopy is a powerful method to obtain spectra of vibrationally excited van der Waals complexes in the ground electronic state even for intramolecular vibrational states above the energy necessary for dissociating of the complex. From comparison with spectra of the bare molecule the complex shift in the fluorobenzene-Argon complex for the ground state was found to be 23 cm^{-1} and the vibrational transitions could be assigned.

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