Rotationally Resolved Ion Dip Spectroscopy of Benzene

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Optical transitions between excited vibrational states in the electronic ground and excited state of benzene were measured with ion dip spectroscopy in a supersonic jet. The observed spectra show clear rotational structure, dependent on the wavelength of the excitation laser and could be simulated by computer calculations.

Ion dip spectroscopy is known to be a powerful method for the analysis of highly excited vibrational states in the electronic ground state, which are not accessible to absorption spectroscopy in supersonic jets.

Introduction

The spectroscopy of vibrations in the electronic ground state can be performed by infrared and Raman spectroscopy. At room temperature these spectra are congested and a separation of overlapping bands in case of large molecules is difficult. Therefore the molecules are studied in a supersonic jet, where the internal degrees of freedom are cooled and the spectra can easily been disentangled. The low density and the short interaction region of the light with the supersonic beam makes an infrared absorption or Raman spectroscopy all but impossible, and therefore the vibrational states of the electronic ground state are determined from wavelength resolved fluorescence spectroscopy. Due to the low fluorescence intensity the resolution of the emission is limited, even with high resolution laser excitation. Higher resolution spectra now can be obtained with fluorescence dip spectroscopy [1] or ion dip spectroscopy [2].

In both cases a resonant electronic intermediate state is populated by a first laser, and the population of this state is probed by a second laser. If this laser frequency coincides with a transition to a vibrational state of the electronic ground state, stimulated emission to this state occurs. The resonant intermediate state will be depopulated and the fluorescence signal or the ion current signal from ionization of this intermediate state will show a dip when the second laser is scanned. However, the observed spectra under high resolution are complicated and have to be analyzed carefully. In a supersonic jet complexes with the seeding gas and clusters of the molecules are readily formed and therefore the ion dip spectroscopy together with mass resolution of the molecules involved allows a unique identification of the spectra. We now have measured the transition from a vibrational state (6^1) in the S_1 state of benzene to the double excited vibrational state (6_2) in the electronic ground state. The complex rotational structure, which is dependent on the excitation conditions, could be understood and simulated. It is seen to be important here not to assign multiple peaks to new transitions, which in fact are subbands and arise from the rotational selection rules.

Experimental

The experimental setup has been described previously [3]. In short, a skimmed supersonic jet with a RETOF mass spectrometer was used. Benzene at 273 K was seeded in He with a backing pressure of 5 bar. The mixture was expanded through a pulsed nozzle of 0.2 mm diameter.

The excitation was performed with two dye lasers (Quanta Ray PDL-1), which were pumped by the third harmonic of a Nd:YAG-Laser (Quanta Ray DCR-1 A).

For the resonant excitation and population of the $S_1 (6^1)$ state of benzene the second harmonic of the first dye laser (Coumarin 307) was used. The frequency doubled light of the second, tunable dye laser (Coumarin 540 A) was used to ionize the molecule and also

stimulate transitions into the ground state. Both laser beams entered the main chamber from opposite directions and were aligned for a common focus by two lenses of 220 mm focal length. The resolution of both dye lasers was about $0.5 \, \text{cm}^{-1}$.

The produced ions were detected with mass selection by a RETOF mass spectrometer with a multichannel plate detector. The ion current was integrated by a boxcar integrator and recorded and averaged by a computer.

Results

In order to measure the ion dip signal we populated the $S_1 \, (6^1)$ state of benzene by a first laser pulse. The population of this state was now probed with a second laser. The wavelength of the laser was chosen such that its wavelength range covers the region of the transition to the $S_0 \, (6_2)$-state. For the identification of the intermediate state, we first scanned the excitation laser with the second laser held at a fixed frequency. The ion current signal then shows the absorption spectrum of this transition and defines the population of the excited state (Figure 1). From this spectrum we obtained a rotational temperature of 4 K in the ground state by computer simulation.

For a first experiment we fixed the wavelength of the excitation laser near the center of the 6_0^1 transition and scanned the second ionizing laser. In this case we obtained a single dip with a width of $1.7 \, \text{cm}^{-1}$, which is smaller than the width of the $S_1 \leftarrow S_0$ transition to the intermediate state, but still larger than the laser bandwidth of $0.5 \, \text{cm}^{-1}$ (Figure 2). At this position the ion dip signal showed the narrowest peak width that we could obtain. This indicates that the width is either given by rotational effects or by broadening of the signal due to the high laser power used for obtaining the dip signal.

Quite a different behavior is obtained if excitation occurs into the wings of the absorption band of the intermediate state (Figure 3). If one leaves the center to either side, two main peaks appeared. At larger offsets one finds two large peaks with a small peak in the center. It is interesting that the distance of the two main peaks is nearly double the offset from the $0-0$ position of the transition to the intermediate state. The shape of the peaks is much different compared to the $S_1 \leftarrow S_0$ resonant transition. The total ion current signal decreased as the wings are excited, but the rela-
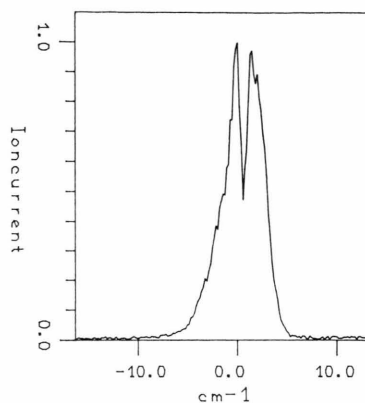

Fig. 1. Ion Current Excitation Spectrum of Benzene in a Supersonic Jet: Pumping to the $S_1 (6^1)$ state.
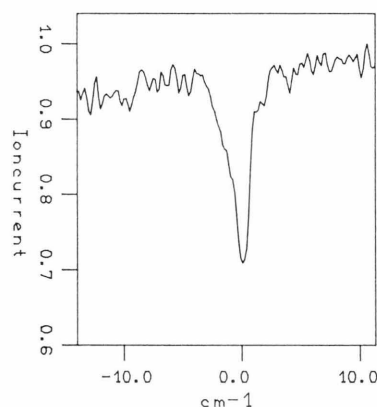

Fig. 2. Ion Dip Spectrum of Benzene in a Supersonic Jet: Resonant excitation to the $S_1 (6^1)$ state and dumping to the $S_0 (6_2)$ state.

tive dip signal stayed constant. At our experimental conditions the ion current signal was lowered by 20% when scanning over a dip. The occurrence of these multiple dips for a single transition has to be explained and analyzed to ensure that there are no other states hidden behind such an intermediate resonant state.

Discussion

In our ion dip experiment we have excited benzene to the $S_1 (6^1)$ state from the vibrationless electronic ground state (Fig. 4) with the first laser. The rotational temperature in the jet is about 4 K and therefore still a reasonably large number of rotational states is ther-
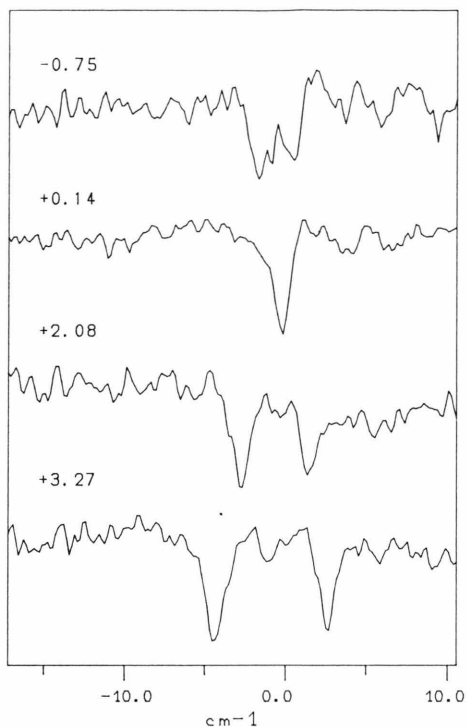
Fig. 3. Ion Dip Spectra of Benzene: Pumping of the resonant state at different wavelengths relative to the origin of the $S_1 (6^1)$ transition. One or more dips at different positions and of changing structure can be seen, depending on the exact position of the pumping wavelength.
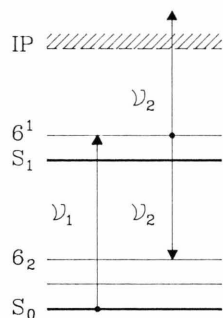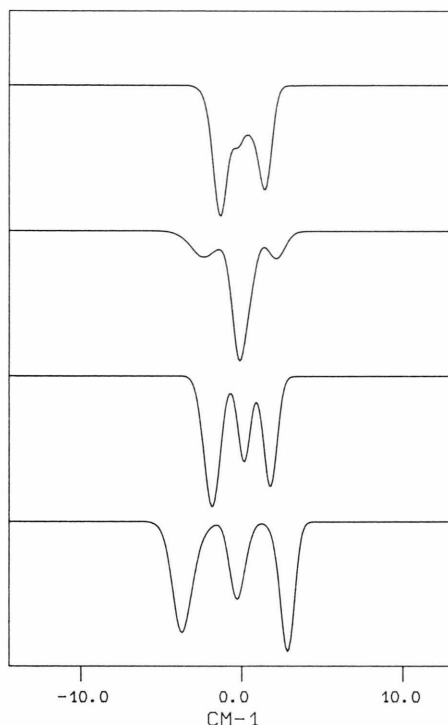

Fig. 5. Calculated Ion Dip Spectra: The calculated spectra correspond to the spectra shown in Fig. 3. The calculation for the benzene molecule was performed for an oblate symmetric top rotor and a rotational temperature of 4 K. The laser bandwidth was set to $0.8 \, \text{cm}^{-1}$ for the simulation of the experimental data.

Fig. 4. Simplified Energy Level Diagram for Ion Dip Spectroscopy: Laser 1 (Frequency v_1) populates the $S_1 (6^1)$ state, which then is probed by ionization with laser 2 (frequency v_2). If v_2 coincides with a transition to the $S_0 (6_2)$ state, stimulated emission to this state reduces the ion current signal.

mally populated. Due to the small rotational constants, the single rotational states cannot be resolved and the pump process populates also a large number of rotational states in the excited state, which is no longer a Boltzmann distribution but is rather depen-

dent on the wavelength of excitation. Excitation in the center of the absorption band, especially in the Q-branch, populates a large number of states, whereas in the wings, which are mainly formed by the P- and R-branches, it mostly populates states with high rotational quantum numbers. The rotational selection rules in this case are given from the fact that we have a perpendicular transition from a nondegenerate ground state to a double degenerate vibrational state in the excited state with a value for the coriolis coupling of 0.6 [4]. For a given temperature we now can calculate the rotational population in the excited state using the selection rules and London-Hönl Factors [5]. The second laser now probes the population in the S_1 state by ionization. A dip in the ion current occurs if the frequency v_2 of the second laser coincides with a transition to the ground state (Figure 4). The probability of stimulated emission is also governed by the rotational selection rules and can be calculated as in the case of the excitation to the intermediate state. The main difference is that we do not have a Boltzmann

distribution in the excited state but a distribution which is highly dependent on the preparation of the intermediate state. The spectra are also more complicated than in the ground state. The simulation has to be performed for a perpendicular transition with rotational selection rules and Coriolis coupling [5] and an l-type doubling [6] of this vibrational state. Computer simulated spectra are given in Figure 5.

For the simulation a rotational temperature of 4 K in the ground state and a laser bandwidth of $0.8\,\text{cm}^{-1}$ was used. The simulation now shows that the multiple dips observed in the ion dip spectra are due to the rotational structure of a single transition, and no further transitions are hidden behind the resonant excitation.

Conclusion

Ion dip spectroscopy is a valuable technique for studying excited vibrational states of large molecules in the electronic ground state, but the observed spectra are often complicated and difficult to explain. From a computer simulation of the rotational structure one can show that the observed multiple dips with a sharp structure, which suggests different vibrational states, are an artifact of the excitation process to the intermediate state and are in fact due to rotational contours. This is especially important if overlapping bands are measured. From two dimensional spectra the nature of the transition can be obtained, and a single state be identified.

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