A study of intermolecular vibrational frequencies of phenol·$(H_2O)_3$ by spectral hole burning spectroscopy

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Abstract

The vibronic spectrum of the phenol·$(H_2O)_3$ complex is obtained by persistent spectral hole burning. The population of the neutral complex is depleted by tuning a hole burning laser to a strong absorption line of the complex. The depopulation is probed by the decrease of fluorescence intensity induced by a second laser. Only transitions which share a common ground state level with the hole burning laser are recorded. Twelve intermolecular frequencies have been found in the region 0–220 cm^{-1} relative to the electronic origin of the complex.

1. Introduction

The technique of spectral hole burning (SHB) in supersonic beams with REMPI and LIF detection has recently been introduced [1,2] to distinguish between different conformers of one species. SHB in combination with time of flight mass selective resonant ionization (REMPI-TOF MS) can be used to distinguish between different sizes, conformers and vibronic levels of clusters [3]. In combination with adiabatic cooling in a supersonic molecular beam spectral hole burning is a powerful tool, comparable to mass selective REMPI-TOF MS but offers the additional advantage to distinguish even between different electronic levels.

Laser-induced fluorescence spectra of a mixture of clusters in a supersonic jet are normally very congested. Even [1+1]-REMPI-TOF MS sometimes lacks absolute mass selectivity because of fragmentation especially of higher, more fragile clusters in the ionic state [4]. These difficulties can be overcome by the use of SHB. We show that this technique can be used to obtain the vibronic spectrum of the phenol·$(H_2O)_3$ complex in the S_1 state. Experimental results concerning other phenol/water clusters will be presented soon.

While Lipert and Colson [3] used REMPI as detection for the depletion, we decided to use laser-induced fluorescence as probe method as described by Wittmeyer and Topp [2]. The probe laser (150 μJ) enters the interaction zone approximately 450 ns after the burn laser (600–800 μJ). This delay time allows spatial overlap of both lasers, while at the same time fluorescence from the burn and probe laser can be distinguished. Spatial and temporal overlap were adjusted to maximal signal depletion. The probe laser is tuned to the origin of phenol·$(H_2O)_3$ to record the fluorescence signal while the burn laser is scanned through the region of interest. The energy of the hole burning laser must be sufficient to deplete the ground state irreversibly to a significant extent. On the other hand nonresonant excitation must strictly be avoided. We found 600–800 μJ sufficient to fulfil these con-

ditions and to obtain holes up to 30% of the fluorescence signal.

2. Experimental

The hole burning spectra have been taken in an apparatus described elsewere [4]. The apparatus consists of a high-vacuum system, an electromagnetically pulsed heatable valve (General Valve Iota One) with 500 μm nozzle hole, and a cooled photomultiplier tube (Thorn EMI 9789). The vacuum was maintained by a $2000 \ \ell \ s^{-1}$ oil diffusion pump (Edwards), backed by a rotatory pump (Leybold Trivac D65B). Pressures are 4×10^{-7} mbar (beam off) and 2×10^{-4} mbar (beam on).

The transition was probed by an excimer laser (Lambda Physik EMG 102) pumped frequency-doubled dye laser (Lambda Physik FL 2002) using the coumarin 153 dye for the wavelength range 274–276 nm. The hole burning laser system consists of an excimer laser (Lambda Physik EMG 200) pumped frequency-doubled (Lambda Physik FL31) dye laser (Lambda Physik FL 3002) using the coumarin 153 dye for the wavelength range 274–276 nm.

The lasers were triggered by a four-channel digital delay generator (Stanford Research DG535) for time delays between 450 and 800 ns. The burn laser is collimated somewhat, so that the colinearly aligned lasers have nearly the same diameter in the image region. The spectra were taken with 11 mbar H_2O and 0.6 mbar phenol seeded in 4000 mbar He at a laser focus/nozzle distance of $X/D = 30$. The signal was recorded by a chart recorder (Philips) after integration with a gated boxcar (Stanford Research SR250). The gate was positioned to record the fluorescence signal of the probe laser.

3. Results and discussion

Stanley and Castleman [5] presented a REMPI spectrum of the $n = 3$ cluster of phenol/water. Because of the high selectivity and sensitivity of spectral hole burning we were able to obtain several new vibronic transitions which clearly belong to phenol·$(H_2O)_3$. Fig. 1 shows the hole burning spectrum of phenol·$(H_2O)_3$ in the region 0–220 cm^{-1}
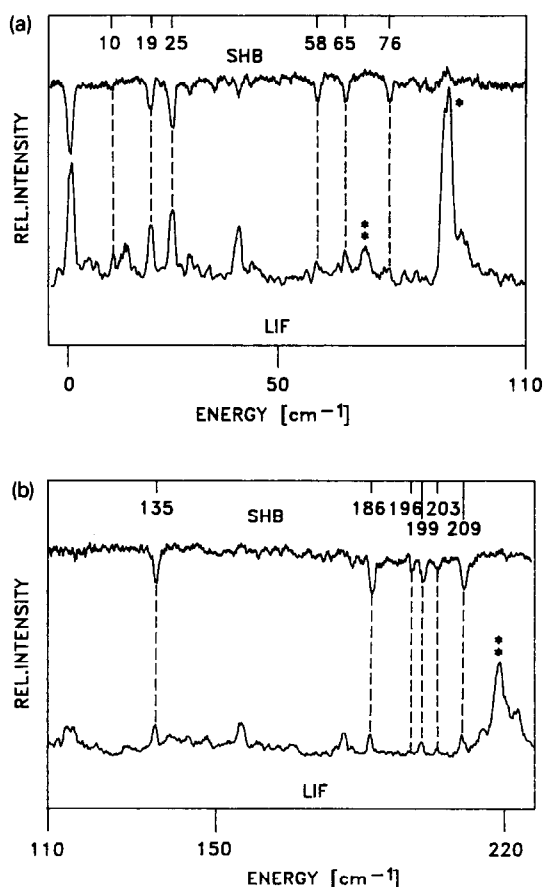

Fig. 1. LIF (lower trace) and SHB (upper trace) spectra of phenol·$(H_2O)_3$ at (a) 0–110 cm^{-1} and (b) 110–220 cm^{-1} relative to the electronic origin. Wavenumber of the probe laser: 36258 cm^{-1}.

blue to the electronic origin (36258 cm^{-1}) of the complex (upper trace) in comparison to the LIF spectrum in the same range (lower trace). The LIF spectrum was recorded by positioning the boxcar gate to the fluorescence of the burn laser.

All holes burned in the fluorescence of the 0,0 transition of phenol·$(H_2O)_3$ can be found in the LIF spectrum. On the other hand many additional features appear in the fluorescence excitation spectrum which do not belong to the $n = 3$ complex. Bands marked with an asterisk can be shown to belong to the phenol monomer and bands with two asterisks to the $n = 1$ complex. All other bands remained unassigned.

The strongest transition in the LIF spectrum is the

electronic origin of the phenol monomer. The small increase of fluorescence intensity in the hole burning spectrum is due to the large amount of fluorescence intensity, caused by the burn laser, which was not accurately separated. Table 1 shows the observed S_1 vibrational frequencies of the phenol·$(H_2O)_3$ complex. The low-frequency transitions for the electronically excited state observed by Stanley and Castleman [5] at 8, 14, 20 and 25 cm^{-1} could be reproduced apart from the features at 8 and 14 cm^{-1}. There is only one transition in this region which belongs to the $n=3$ complex, a weak band at 10 cm^{-1}. This range was recorded again with higher sample rate and better S/N, but no other features could be found.

A cyclic structure can be assumed for phenol·$(H_2O)_3$ as calculated for the p-cresol·$(H_2O)_3$ cluster (STO-3G basis) [6] in which one water molecule acts as proton acceptor, the other as donor and the third bridging them both. The 186

cm^{-1} band in this cyclic cluster can probably be assigned to the intermolecular stretching mode of the acceptor water molecule on the basis of similar features in the p-cresol/water system [7]. The 135 cm^{-1} band may correspond to an intermolecular wag vibration of the acceptor water molecule, but this remains speculative until a complete normal coordinate analysis has been performed. Four of the frequencies shown in Table 1 may arise from combination transitions, but it cannot been excluded that they arise from intermolecular fundamental vibrations.

All transitions found in the hole burning spectrum of phenol·$(H_2O)_3$ belong to this cluster. Furthermore it can be excluded that any of them arise from hot bands.

4. Acknowledgement

5. References

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Table 1.
Observed frequencies of phenol·$(H_2O)_3$ and possible assignments

Rel. frequency (cm^{-1})	Assignments
0 (36258)	origin phenol·$(H_2O)_3$
10	ξ_1
19	ξ_2
25	ξ_3
58	ξ_4
65	ξ_5
76	ξ_6
135	ξ_7
186	ξ_8 stretching mode σ
196	$\xi_8+\xi_1$?
199	$\xi_9/\xi_7+\xi_5$?
203	$\xi_8+\xi_2$?
209	$\xi_{10}/\xi_8+\xi_3/\xi_7+\xi_6$?