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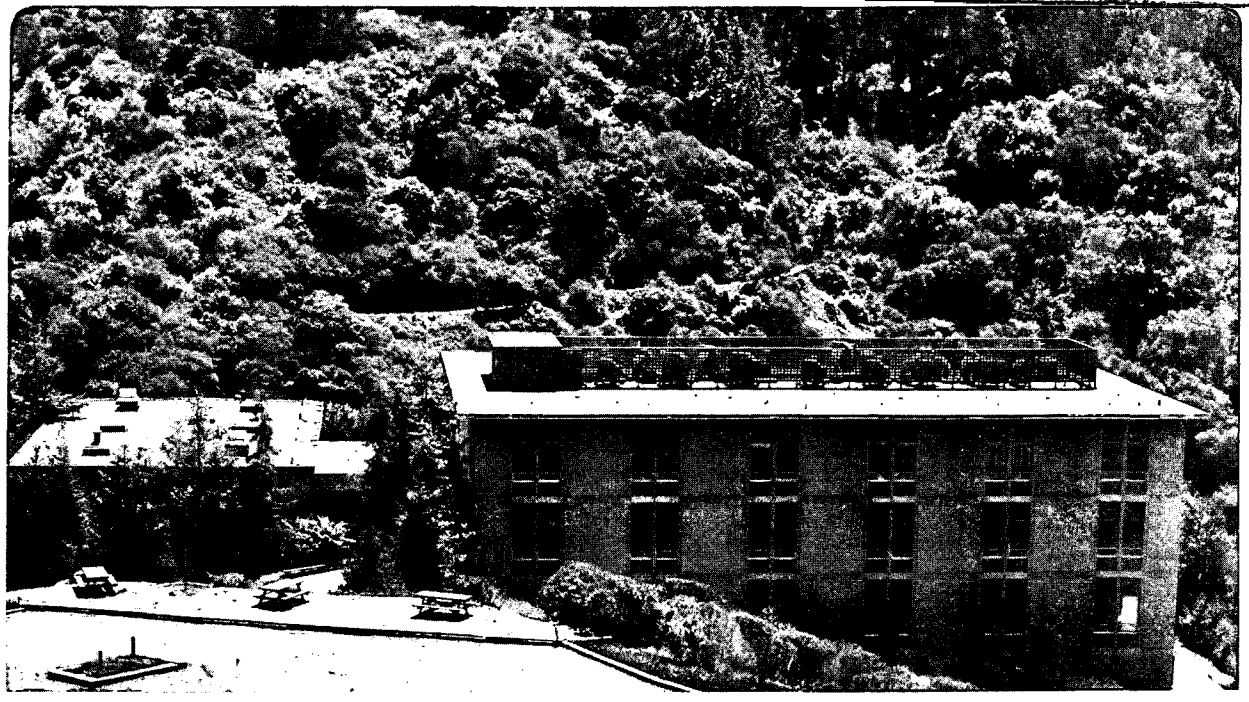

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DISCLAIMER

Infra-red Predissociation Spectra of Water Dimer in a Supersonic Molecular Beam

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ABSTRACT

The infra-red absorption spectrum of the hydrogen-bonded water dimer, $(H_2O)_2$, formed in a supersonic expansion, was recorded in the region of the OH stretch by monitoring the predissociation resulting from the absorption of the radiation. The conditions were such that there was minimal contribution to the observed spectrum from higher water polymers. The observed features show considerable structure, with widths that appear to be limited by the optical resolution of 2 cm^{-1}. A combination band of the OH stretch with the water bend and an overtone of the bending vibration were also observed.

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INTRODUCTION

The previous investigations of the infrared vibrational spectra of water clusters in the gas phase[1] had shown that the dimer spectrum differs markedly from that of the higher polymers, and was also distinctively different from the absorptions in bulk liquid water. However, the beam conditions and laser resolution were such that few conclusions could be drawn about the possibilities of obtaining high resolution vibrational spectra of the dimer.

Accurate information about the ground state of $(H_2O)_2$, is available from the molecular beam electric resonance (MBER) work of Dyke et al.[2] The microwave and radiofrequency transitions observed show that the ground state structure is trans-linear, with a linear hydrogen bond, in contrast to the higher polymers which have a cyclic structure. The B value of the almost symmetric top could be accurately determined ((B+C)/2 = 6160.7 MHz), but the A constant is less certain (approximately $7cm^{-1}$). From the centrifugal distortion constants Dyke et al. estimated that the hydrogen stretching vibration of one water molecule against the other occurs at about 140 cm^{-1}.

A better knowledge of the vibrational spectrum of the dimer would give much needed information on the properties of the hydrogen bond, and the influence of hydrogen bonding on the donor and acceptor units. While some information is available from matrix studies, the matrix certainly precludes the possibility of obtaining much structural information because the rotational spectrum is supressed. The aim of this work was to investigate the water dimer spectrum under conditions in which there was minimal

contamination of the spectrum by higher polymers and at sufficient resolution to indicate if the rotational transitions could be observed, or if in fact predissociation linewidth would be larger than the rotational spacing. The observation of the $(HF)_2$ spectrum at high resolution in a gas cell[3] indicated that the former possibility was very likely.

EXPERIMENTAL

The water dimers were formed in a supersonic expansion through a nozzle of 50 micron diameter, of helium at pressures from 1 to 4 atm, which had bubbled through a water reservoir held at a temperature of 15, 25 or 35°C. The nozzle was held at a temperature of 90°C to prevent condensation of the water vapor. After two stages of differential pumping and a flight path of about 0.15 m, the molecular beam was ionized by an electron bombardment ionizer and the resulting ions mass analyzed with a quadrupole mass spectrometer. The $(H_2O)_2$ fragmented in the ionizer to give predominantly the relatively stable H_3O^+ ion and so the dimer is detected at mass 19. The beam conditions were such that the amount of trimer present in the beam was kept very low. A measure of the trimer content of the molecular beam is given by the ratio of the mass 19 signal to that at mass 37 (this is only approximate because of the uncertainty in the fragmentation patterns), and this indicates that the dimer to trimer ratio was better than 20:1.

1 mj, 10 nsec pulses of tunable infrared radiation at about 2 cm^{-1} resolution and 10 Hz repetition rate were obtained from an optical parametric oscillator (OPO) of the Byer design[4] pumped by a Quanta Ray Nd:YAG laser in the far field. Damage to the optical components prevented the oscillator from running at the higher resolution that would be obtained by the use of intracavity line-narrowing elements. The wavelength calibration was performed using a monochromator.

The infra-red radiation overlaped the molecular beam in an anti-parallel direction, and was brought to a focus near the nozzle. This is not an ideal arrangement because it leads to non-uniform power density along the molecular beam however, the optical properties of the OPO beam were such that a narrow parallel beam was almost impossible to produce. Over most of the interaction region the laser beam had a slightly larger diameter than the molecular beam, which ensured that all of the molecular beam that was sampled by the ionizer could have interacted with the radiation.

The energy contained in an OH stretch is considerably greater than that required to break the hydrogen bond, and so upon absorption of such an energetic infrared photon, the dimer molecules predissociate, consequently reducing the number of water dimers reaching the detector. The experiment is performed by scanning the infra-red radiation while looking for a depletion or "hole burning" in the mass 19 signal. The recorded signal is accumulated for between 2000 and 4000 laser shots at each wavelength. The power of each laser shot was recorded and used to normalize the depletion signal to the laser power. Since the spectra of interest lie in regions of very high atmospheric water absorption, the whole optical path from the OPO to the window into the molecular beam vacuum system had to be continuously flushed with dry nitrogen.

Spectra were recorded from 3500 to 3900 cm^{-1} and around 3200 cm^{-1} and 5300 cm^{-1}. No spectra could be recorded between 3450 and 3500 cm^{-1} because the OH impurity in the $LiNbO_3$ crystal of the OPO caused the output power to be anomalously low in this region.

The power dependence of the major peaks was checked and found to be linear within the accuracy of the measurements.

Any problems that the focusing of the radiation onto the nozzle might have produced could be investigated since the dimer signal arriving at the nozzle was "time resolved", using a multi-channel scaler with a 1 microsecond channel width. The laser pulse is only about 10 ns long, which means that the arrival time at the detector of the molecules that interact with the radiation translates directly into the position of the dimer molecules along the molecular beam, whose velocity is about 1 mm/sec, when the molecule absorbed the radiation.

No such "nozzle" effect was observed in the idler range, but in the more intense signal range an apparent decrease in the dimer population at the nozzle could be seen. This did not affect the molecules down stream, which had already left the nozzle before the laser pulse arrived. It does indicate that in the high density region just in front of the nozzle the signal beam is strongly absorbed over a wide frequency range.

RESULTS

The water dimer absorptions in the OH streching region that we observed are shown in Figure 1. An assignment that is in reasonable agreement with the matrix isolation spectra[5] is possible if the shoulder on the low frequency side of the 3730 cm^{-1} absorption is taken to be the v_3 of the donor. The main peaks in the spectrum are respectively assigned as v_1(donor) at 3545 cm^{-1}, v_1(acceptor) at 3600cm^{-1} ,v_3(acceptor) at 3730cm^{-1} and v_3(donor) at 3715 cm^{-1}, and are compared to the matrix values in Table 1. Some of the vibrations recorded in this work are shifted by more than 20 cm^{-1} form the matrix results.

Over the range of stagnation pressures used (from less than 1 atm to greater than 4 atm) the 3730 and 3600cm^{-1} bands become significantly narrower with increasing pressure. This is consistent with the increased degree of cooling in the harder expansions. If large amounts of higher polymers were present in the beam then we might have expected to see a large linewidth at higher pressure as these conditions are more favorable for the formation of the polymers. The structure on the 3550cm^{-1} band is reproducible; however, because of the unknown, though low rotational temperature (estimated to be about 10K), the apparent perpendicular band nature of this feature can not be conclusively substantiated. That this molecule should show perpendicular and/or parallel bands could be expected since it is very nearly a symmetric top, with the top axis lying along the hydrogen bond and defined by the two oxygen atoms.

The existence of the rotational structure in the gas phase spectrum makes it difficult to compare the peak intensities with the matrix work.

The peaks to the high and low frequency sides of the 3730 cm^{-1} band are almost certainly combination bands arising from combinations of the v_1 modes of the donor and acceptor molecules with the low frequency vibrations of the hydrogen bond. Theoretical calculations[6] and the MBER data indicate that the stronger bands at 3753, 3760 and 3778 cm^{-1} should be assigned to combinations involving the hydrogen bond stretch, the out of plane bending of the hydrogen bond and the in plane bending of the hydrogen bond, respectively. If this is the case then these modes are lowered by about 10 cm^{-1} when the OH stretches in the water molecules are excited. This vibrational shift would cause the diagonal hot bands to be displaced from the fundamental and may account for the greater width of the 3550 cm^{-1} band. This band would be expected to be more profoundly influenced by the water - water stretching motion since it mainly involves the stretching of the hydrogen-bonded hydrogen.

While the assignment of these side peaks to combination bands seems reasonable, it can not be completely ruled out that they arrise from absorption of other complexes such as $(H_2O)_3$ or $(H_2O)_2He_n$.

Weak absorptions were observed at 3186cm^{-1} and 5333cm^{-1}, which were assigned to combinations of two HOH bends (v_2 modes) and an OH stretch with an HOH bend, respectively. Owing to signal to noise limitations only a single absorption could be observed in each region. Even so this data is consistent with the OH stretching frequencies being reduced upon forming the hydrogen bond while the bending vibrations are stiffened.

This work indicates that it is possible to obtain infrared spectra of the water dimer free of contamination from higher polymers. The spectrum shows a rotational envelope and it is likely that with increased resolution the rotational structure can be recorded; this would greatly enhance the feasiblility of obtaining structural information on the vibrationally excited states of the water dimer.

ACKNOWLEDGMENT

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Table 1

Stretching vibrations of $(H_2O)_2$ / cm^{-1}

	N_2 Matrix[3]	This work
Acceptor		
ν_1	3627.2	3600
ν_3	3715.0	3730
Donor		
ν_1	3550.0	3545
ν_3	3698.8	3714

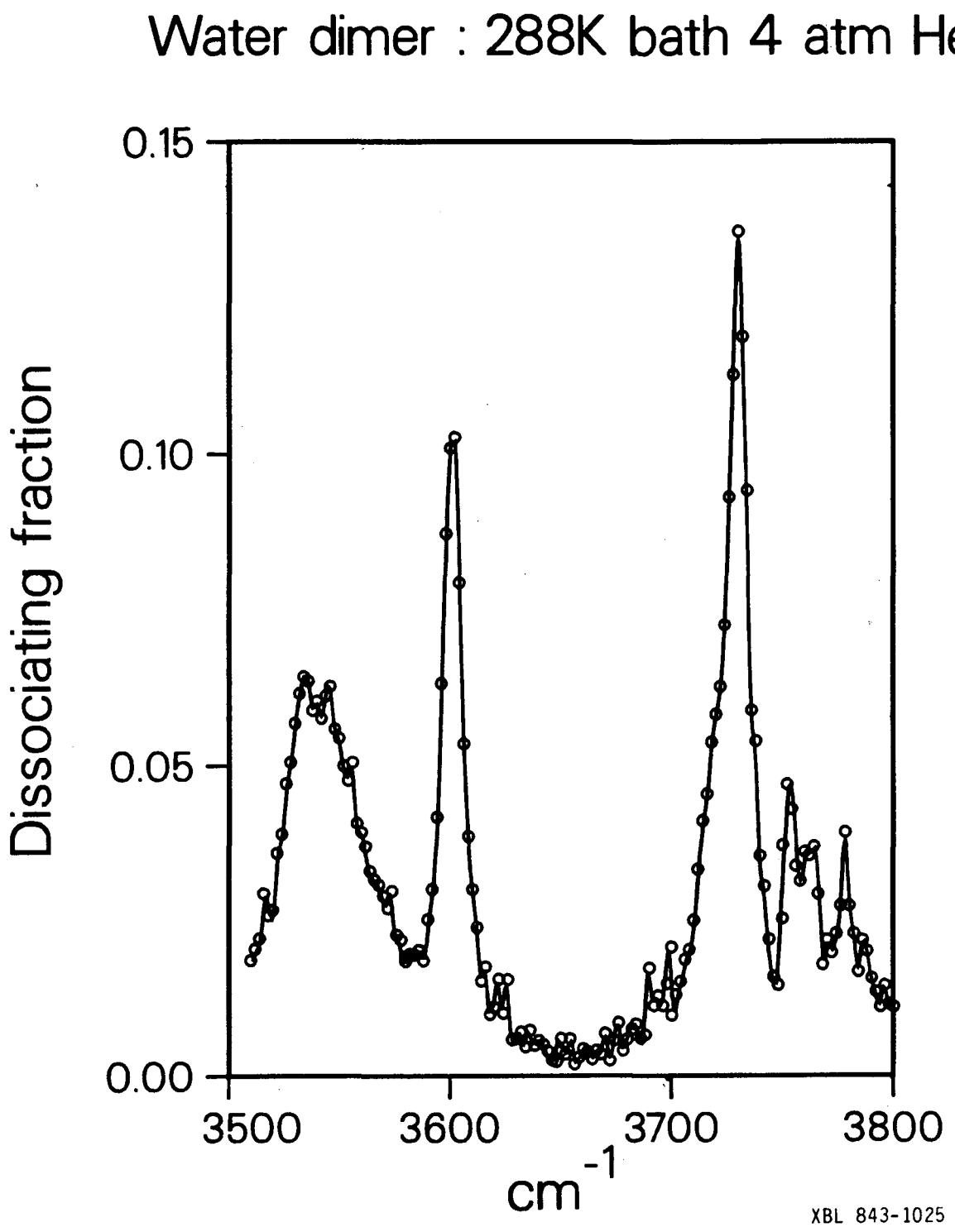
Water dimer : 288K bath 4 atm He
Dissociating fraction
0.15
0.10
0.05
0.00
3500
3600
3700
3800
cm -1
XBL 843-1025

Fig. 1

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