



Infrared spectroscopy of water clusters co-adsorbed with hydrogen molecules on a sodium chloride film



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ABSTRACT

Hydrogen gas containing a trace of water vapor was dosed on a vacuum-evaporated sodium chloride film at 13 K, and water clusters formed on the substrate were investigated by infrared absorption spectroscopy. Absorption bands due to $(\text{H}_2\text{O})_n$ clusters with $n = 3\text{--}6$ and an induced absorption band due to hydrogen were clearly observed. With increasing gas dosage, the intensities of the cluster bands increased linearly while the intensity of the hydrogen band was constant. This suggests that the water clusters were formed in two-dimensional matrices of hydrogen. We found that the water clusters did exist on the surface upon heating even after the hydrogen molecules had desorbed. A further rise of the substrate temperature up to 27 K yielded the formation of larger clusters, $(\text{H}_2\text{O})_n$ with $n > 6$. We also discuss the origins of the two bands of the trimer in terms of pseudorotation and a metastable isomer.

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1. Introduction

Elucidating the nature of the hydrogen bond interaction is essential for precise descriptions of water vapor, liquid water, and ice. Since small water clusters provide simple stages for investigation of the hydrogen bond, their stable structures and states of vibration, rotation, and proton tunneling have been extensively studied. While in the dimer one of the water molecules acts as the proton-donor and the other as the acceptor [1], the most stable structures of the trimer, tetramer, and pentamer have been found to be the cyclic ones, where each water molecule plays both the roles of the donor and acceptor. As for the hexamer, on the other hand, several kinds of isomers with slightly different energies of formation have been predicted by *ab initio* calculations [2–6], such as the cage, cyclic, and book ones. Whereas the cyclic isomers of the tetramer and hexamer have the S_4 and S_6 symmetries, respectively, those of the trimer and pentamer belong to the C_1 symmetry. Each of the latter two clusters therefore has inequivalent components with the same minimum energy, but was nevertheless revealed to be the symmetric top by far infrared spectroscopy owing to rapid pseudorotation [7,8].

Because the matrix isolation technique has an advantage in isolating and fixing water clusters, infrared spectra of water

clusters have been measured in various matrices of Ne [9–11], Ar [11–16], Kr [14,16], Xe [16,17], para- H_2 [11,18], D_2 [19], and N_2 [20]. Through these studies, dependence of the intra-molecular vibrational frequencies of water clusters on the matrix species has got clear. We point out that the matrix species used in previous studies described above were infrared inactive. This is probably because the matrix species are required to be inert. However, spectroscopic observations of matrices in addition to water clusters may supply information on the trapping structures of the clusters in it.

In the present study, a mixed gas of water vapor and hydrogen was dosed on a porous NaCl film, and both water- and hydrogen-related vibrations were measured with Fourier transform infrared spectroscopy as functions of the gas dosage and substrate temperature. It was found that water clusters were formed in two-dimensional (2D) hydrogen matrices on the NaCl film. The increase of the gas dosage resulted in increased absorption band areas of the water clusters but left the area of the hydrogen band constant. As the substrate temperature was raised, the cyclic tetramer and pentamer were formed from the trimer. In addition, we succeeded in detecting water clusters isolated on the NaCl film without hydrogen, using its desorption on temperature rise. The production of isolated water clusters on a surface has a significant meaning in terms of the study on the reaction of water clusters and other molecules. After further heating of the substrate, new absorption bands appeared in the bonded-OH vibration region. We attribute them to larger clusters, $(\text{H}_2\text{O})_n$ with $n > 6$.

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2. Experimental

The experimental set-up consists of a vacuum chamber (base pressure: 2×10^{-8} Pa) equipped with a liquid helium cryostat, a gas handling system, a FTIR spectrometer (Nicolet Magna IR 550), and a compartment of a liquid-nitrogen-cooled HgCdTe detector. A $10 \times 10 \times 1$ mm³ single crystal of CaF₂ (111) (Furuuchi Chemical Corp.) was used as the substrate, and was mounted on a copper block connected to the cryostat. Temperature of the substrate were measured by a silicon diode (model DT670-SD, Lake Shore, Inc.) mechanically fixed on it. A fragment of a NaCl single crystal (Furuuchi Chemical Corp.) was inserted into a helical tungsten filament, and was then vacuum-evaporated onto the CaF₂ substrate maintained at 16 K. The rate and amount of evaporation monitored by a quartz oscillator were 2 layers per second and 200 layers, respectively. Note that these are the effective values since a deposited NaCl film is known to be highly porous [21]. After evaporation the NaCl film was annealed at 64 K.

The copper block had a circular hole with a diameter of 8 mm in order for FTIR spectroscopy in the transmission configuration. The whole optical path was purged with a constant flow of dry nitrogen to eliminate water vapor and carbon dioxide in the atmosphere. Infrared spectra were recorded at a resolution of 4 cm⁻¹. We used hydrogen gas (Takachiho Chemical Industrial Co., Ltd.) with a purity of 99.99995% and ultrapure water (Milli-Q, Yamato Scientific Co., Ltd.). The hydrogen gas containing a trace of water vapor was prepared in the gas handling system and was dosed on the NaCl film maintained at 13 K through a pulse valve whose orifice has a diameter of 0.76 mm. The stagnation pressure was 5×10^4 Pa, and the pulse duration we used ranged from 1 to 30 ms. The gas dosage was expressed by the total open time of the pulse valve.

3. Results

3.1. Exposure dependence of the infrared spectrum

Fig. 1 shows dependence of the infrared spectrum on the duration of exposure. A broad absorption feature extending from 3000 to 3600 cm⁻¹ is due to amorphous ice. A band at 4128 cm⁻¹ is attributed to induced infrared absorption of hydrogen. Ortho- and para-hydrogen, whose Q branches, Q(1) and Q(0), have the transition energies of 4161 and 4155 cm⁻¹ in the gas phase, respectively [22], are not spectroscopically resolved. Absorption peaks above (below) 3600 cm⁻¹ are due to the free- (bonded-) OH stretching vibrational modes. When we dosed a pure gas of water vapor without hydrogen onto a NaCl film, these peaks of the water clusters were absent, and only the broad band of amorphous ice was observed. Thus, hydrogen molecules play a role in producing water clusters isolated from each other. The bands at 3368 and 3335 cm⁻¹ in Fig. 1 are attributed to the cyclic- (cyc-) tetramer and cyc-pentamer, respectively, based on the reported assignments in the gas phase [23,24], solid neon [10], and solid para-hydrogen [18] studies. Both the bands at 3531 and 3503 cm⁻¹ are assigned to the trimer while the band at 3228 cm⁻¹ is attributed to the hexamer. A detailed discussion of these bands will be given in the Discussion section. The bonded-OH vibrational frequencies of the clusters are practically independent of the amount of exposure. Our assignments are summarized in Table 1. The band frequencies of (H₂O)_n with $n = 3-6$ show red shifts from the gas phase values. The magnitudes of the shifts in the present study are comparable to those in solid para-H₂ [18].

Note that the infrared absorption feature of the dimer is absent. By evaluating the noise level around 3579 cm⁻¹, where the dimer

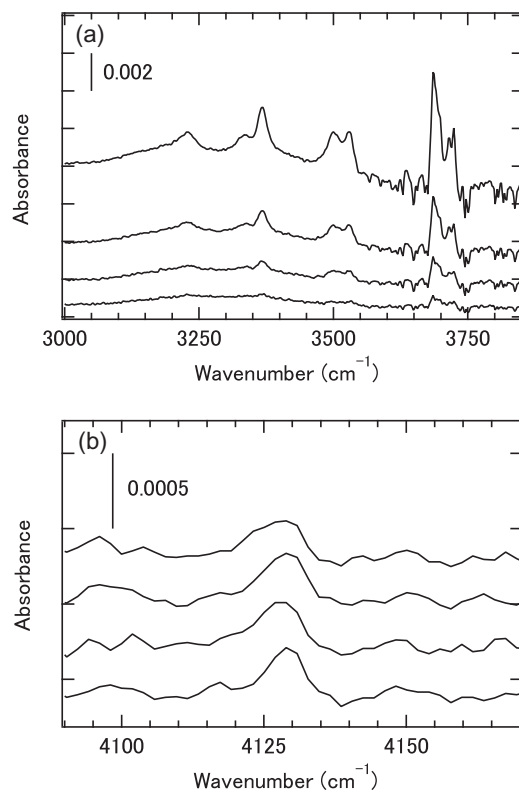


Fig. 1. Infrared spectra at 13 K in the regions of (a) OH stretching vibration of water clusters, and (b) stretching vibration of hydrogen. From the bottom to the top, spectra correspond to the exposures of 10, 70, 140 and 295 ms, respectively.

Table 1

Frequencies (cm⁻¹) of the bonded-OH stretching vibrational modes of (H₂O)_n clusters with $n = 2-6$ in the gas phase [23], in solid para-H₂ [18], and on the NaCl film. $\Delta\nu$ indicates the frequency difference between the absorption band observed in solid para-H₂ and that on the NaCl film: $\Delta\nu = \nu_{\text{NaCl}} - \nu_{\text{pH}_2}$. As for the trimer, the average frequency of the two bands is used.

Assignment	Gas phase	3D solid pH ₂ ^a	NaCl film (this work)	$\Delta\nu$
(H ₂ O) ₂	3601 ^b	3579	–	–
(H ₂ O) ₃	3533 ^b	3531, 3518	3531, 3503	–8
Cyc-(H ₂ O) ₄	3416 ^b	3379	3368	–11
Cyc-(H ₂ O) ₅	3360 ^b	3338	3335	–3
(H ₂ O) ₆	3220 ^c	3222	3228	+6

^a Fajardo (2001) [18].

^b Huisken (1996) [23].

^c Paul (1997) [24].

band was observed in solid para-H₂, and using the infrared intensity of the bonded-OH vibration of the dimer, 330 km/mol, calculated at the B3LYP/6-311++G** level [25], we find that the dimer column density is 6.1×10^{13} cm⁻² at most after 295 ms exposure. In a similar way, estimation of the spectral noise around 3770 cm⁻¹, where an absorption band due to the rotating monomer is possibly buried, and citation of the infrared intensity of the monomer antisymmetric vibration, 57 km/mol, calculated at the B3LYP/6-311++G** level [25] yield the upper limit of the rotating-monomer column density of $\sim 1.5 \times 10^{15}$ cm⁻² after 295 ms exposure.

The integrated intensities of the absorption bands obtained by gaussian-fitting are plotted as a function of the exposure in Fig. 2. The integrated intensity of the hydrogen band is nearly constant. The constant value derived from fitting is 2.6×10^{-3} cm⁻¹. On the other hand, the band areas of the clusters show linear increases. In order to obtain the growth rates of the column densities on the film, the slope values of the fitted lines are divided by

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