Infrared Studies of the Librations of Water Molecules in the Solid Matrices at 20°K

By Tatsuo MIYAZAWA

(Received July 28, 1960)

The matrix isolation technique has been applied for the infrared absorption studies in the rocksalt or potassium bromide regions[1-4], however, not in the cesium iodide region so far. In the cesium iodide region (400∼190 cm^{-1}) librational frequencies of small molecules in the crystalline state as well as internal rotation frequencies and bending frequencies are observed. These intramolecular vibrations are coupled with rotational motions in the vapor phase and quite complicated vibration-rotation bands are observed. In the solid matrices at sufficiently low temperatures, however, translational diffusion as well as rotational diffusion of trapped molecules are generally hindered, and the overall rotational motions are reduced to librational motions. No rotation envelope is apparent, and complicating effects frequently arising from rotational motions in the vapor phase are absent.

In carrying out matrix isolation experiments it is necessary to purify the matrix material carefully since the molar ratio (M/R) of the matrix (M) and the reactive species (R) may be as high as 1000 or more. It is not possible to remove the trace of water in nitrogen gas by simply passing the gas through a liquid nitrogen bath. It was necessary first to measure the spectra of water in the nitrogen matrix at various M/R ratios. Spectroscopic studies of water itself are also interesting in relation with hydrogen bonds and with the effects of matrix solids on the low frequency vibrations.

Experimental Results

For spectroscopic measurements in the region 400∼190 cm^{-1} a Perkin Elmer Model 12C spectrometer was used with the cesium iodide optics[5]. The experimental technique of the matrix isolation method has been described[1]. The infrared spectra of water in the solid nitrogen matrix at 20°K were measured for the molar ratios (N_2/H_2O) of 1000, 200, 80 and 40. In each case 55 micromoles of water was dispersed in the matrix over an area of about 2 cm^2. The nitrogen gas used in the measurement was purified by being passed over copper at 600°C and then through a liquid nitrogen bath. The observed spectra are shown in Fig. 1. It may be seen that the intensity of the band at 218 cm^{-1} increases as M/R is increased from 40 to 1000. The intensity of the band at 243 cm^{-1} increases as M/R is increased from 40 to 80, reaches its maximum for M/R of 80∼200 and then decreases as M/R is increased to 1000. The band at 265 cm^{-1} appears to exhibit its intensity maximum for M/R of 200.

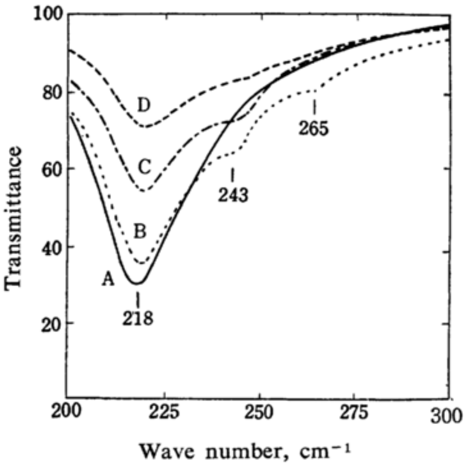

Fig. 1. Infrared spectra of water in the solid nitrogen matrix at 20°K. A: M/R =1000, B: M/R=200, C: M/R=80, D: M/R=40.

In order to measure the effect of isotopic substitution on the water bands, 55 micromoles of heavy water was also suspended in the solid nitrogen matrix for M/R of 200; however, in this case no bands were observed in the region above 190 cm^{-1}.

The infrared spectrum of water (55 micromoles, M/R of 200) was also measured in the solid argon matrix at 20°K. Argon gas was

---

[1] E. Whittle, D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1943 (1954); E. D. Becker and G. C. Pimentel, ibid., **25**, 224 (1956).

[2] M. Van Thiel, E. D. Becker and G. C. Pimentel, ibid., **27**, 486 (1957).

[3] E. Catalano and D. E. Miligan, ibid., **30**, 45 (1959).

[4] M. Van Thiel, E. D. Becker and G. C. Pimentel, ibid., **27**, 95 (1957); G. C. Prinental, *Spectrochim. Acta*, **12**, 94 (1958); T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).

[5] T. Miyazawa, ibid., **29**, 421 (1958). The measurements were made at the University of California.

purified by being passed over copper heated to 600°C and then through a dry ice-acetone bath. In this case no bands were observed in the region 400~190 cm^{-1}, in contrast with the case of the nitrogen matrix.

Discussion

Infrared spectra of water in the solid nitrogen matrix have been measured in the region 3500~3000 cm^{-1} by Van Thiel, Becker and Pimentel[2]. Eleven peaks have been observed at various M/R ratios, and the bands at 3725 cm^{-1} and 3627 cm^{-1} have been assigned to the monomeric species, and the other bands have been assigned to the dimeric, trimeric, and polymeric species.

Assignment of Low Frequencies. — In the present study in the cesium iodide region three bands were observed at 218, 243 and 265 cm^{-1}. The intensity of the band at 218 cm^{-1} is plotted against M/R in Fig. 2, along with the corresponding curve for the 3725 cm^{-1} band. It may be seen that the intensity of the 218 cm^{-1} band changes in iust the same manner as the intensity of the 3725 cm^{-1} band of the monomeric species. The 218 cm^{-1} band is therefore assigned to the monomeric species. The 243 cm^{-1} band is observed as a shoulder of the 218 cm^{-1} band and its intensity change with M/R appears to correspond most closely with the 3691 cm^{-1} band of the dimeric species[2].

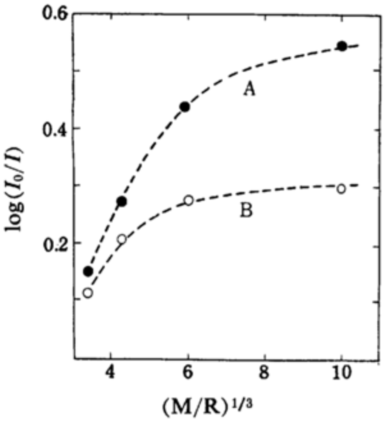

Fig. 2. Peak intensities vs. $(M/R)^{1/3}$.
A: 218 cm^{-1}, B: 3725 cm^{-}.

218 cm^{-1} Band of Monomer.—All the intramolecular vibrations of the monomeric species have already been observed[2] at 3725, 3627 and 1600 cm^{-1}. The 218 cm^{-1} band is, therefore, undoubtedly due to translational or rotational modes in the solid matrix. The translational and rotational motions are restricted in the matrix and become vibrational motions giving rise to vibrational infrared bands.

Lattice Vibrations of Ice. — Prior to more detailed discussions of the matrix spectra the infrared bands of crystalline ice due to these translational or rotational vibrations will be briefly reviewed. The infrared bands due to the translational lattice vibrations of water and heavy water (at −190°C) have been observed at 229 and 222 cm^{-1} respectively[6]. The observed frequency ratio (ν_{H_2O}/ν_{D_2O}) of 1.03 agrees with the theoretical ratio of $1.05=(M_{D_2O}/M_{H_2O})^{1/2}$ for the translational mode. On the other hand the rotational lattice vibrations (librations) of water and heavy water (at −170°C) have been observed at 850 and 630 cm^{-1} respectively[7] and in this case the frequency ratio of 1.35 is much greater than the ratio of 1.03 for the translational mode.

Three Librations in the Nitrogen Matrix.— The 218 cm^{-1} band in question disappears on deuteration and the corresponding band of heavy water has not been observed in the region above 190 cm^{-1}. The isotopic frequency ratio for this mode is definitely greater than the ratio of 1.05 expected for the translational mode. The 218 cm^{-1} band may thus be assigned to a librational mode of the monomeric species in the nitrogen matrix.

So far we have not specified the types of librations in the matrix. For the monomeric species of water there are three types as shown in Fig. 3; one around the twofold axis (the B axis), one around the axis perpendicular to the molecular plane (the C axis), and the last one around the axis of the least moment of inertia (the A axis). The first one will not be infrared active since the B axis is parallel to the dipole moment of the molecule. The other two involve rotations of the molecular dipole moment and will give rise to strong infrared bands.

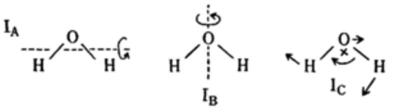

Fig. 3. Librational modes of monomer.

Intensity of Libration Bands.—The infrared intensities of these libration bands may be estimated assuming that the molecules carry out librations about the axes passing through the center of the mass. The moments of inertia about the three axes are

$$I_A=2m_Hr^2(m_O/M_{H_2O})\cos^2\alpha$$

$$I_B=2m_Hr^2\sin^2\alpha$$

---

[6] R. Zimmermann and G. C. Pimentel, unpublished.

[7] K. B. Harvey and P. A. Giguère, *Can. J. Chem.*, **34**, 798 (1956); N. Ockman, *Advances in Physics*, **7**, 199 (1958); D. F. Hornig, H. F. White and F. P. Reding, *Spectrochim. Acta*, **12**, 338 (1958).

and $I_C = I_A + I_B$

where m_H and m_O are the masses of the hydrogen and oxygen atoms, respectively, r the bond length and 2α the interbond angle. Now if the monomeric species is randomly oriented in the matrix the infrared intensities, D_A and D_C, of the A and C librations are expressed analogous to the vapor intensities, and

$$D_i \propto |\partial\mu/\partial Q_i|^2 = |\partial\mu/\partial\theta_i|^2 \cdot |\partial\theta_i/\partial Q_i|^2 = \mu^2/I_i$$

where μ is the dipole moment, Q_i the ith normal coordinate, θ_i the angle of rotation around the ith axis, and I_i the corresponding moment of inertia. The intensity ratio of the A and C bands is calculated to be $D_A/D_C = 2.7$ for the H_2O molecule with the bond angle of 105°. The 218 cm^{-1} band of the monomeric species is considered to be primarily due to the A librational mode.

Librational Frequencies. — The three librational frequencies may be estimated assuming that the potential energy arises from Cartesian displacements of the hydrogen atoms in the matrix. The potential energy possibly arising from Cartesian displacements of the oxygen atom was not considered in the present treatment. The Cartesian displacements of the hydrogen atoms, ξ_A, ξ_B and ξ_C, due to the rotations around the three axes are

$$\xi_A = \theta_A (m_O/M_{H_2O}) r \cos\alpha$$

$$\xi_B = \theta_B r \sin\alpha$$

and

$$\xi_C = \theta_C r [\sin^2\alpha + (m_O/M_{H_2O})^2 \cos^2\alpha]^{1/2}$$

Taking into account the potential energies for the two hydrogen atoms, the librational frequencies, ν_A, ν_B and ν_C, are found to be

$$(2\pi\nu_A)^2 = (K/m_H)(m_O/M_{H_2O})$$

$$(2\pi\nu_B)^2 = (K/m_H)$$

and

$$(2\pi\nu_C)^2 = (K/m_H)\{\tan^2\alpha + (m_O/M_{H_2O})^2\}/\{\tan^2\alpha + (m_O/M_{H_2O})\}$$

whre K is the potential constant. The value of K is calculated to be 0.032 millidyne/A from the ν_A frequency (218 cm^{-1}) of water, and other librational frequencies were calculated to be $\nu_B = 231$ and $\nu_C = 226\ cm^{-1}$ for H_2O and $\nu_A' = 146$, $\nu_B' = 164$ and $\nu_C' = 157\ cm^{-1}$ for D_2O.

The ν_C frequency of 226 cm^{-1} is slightly higher than the observed ν_A frequency of 218 cm^{-1} and the intensity of the ν_C band is considered to be weaker than the intensity of the ν_A band as mentioned before. In fact the 218 cm^{-1} band has an ill-defined shoulder on the high frequency side around 230 cm^{-1}, in agreement with the result of the present treatment[*]. The librational frequencies calculated for D_2O are much lower than 190 cm^{-1}, again in agreement with the result of the present measurement on D_2O.

243 cm^{-1} Band of the Ring Dimer. — The structure of the dimeric species of water in the solid nitrogen matrix has been found to be a ring dimer by Van Thiel et al.[2] The ring dimer has a center of symmetry and there will be three infrared active low frequency vibrations as shown in Fig. 4. The b_u vibration involves the stretching of the O···H hydrogen bonds and its frequency will be appreciably higher than the two a_u frequencies involving only the bending of the hydrogen bonds. The observed frequency of 243 cm^{-1} is slightly higher than the monomeric frequency and this is most probably due to either one of the two a_u modes of the ring dimer.

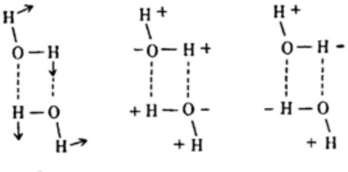

Fig. 4. Infrared active low frequency modes.

Libration in the Argon Matrix. — The librational frequencies of water in the argon matrix have not been observed in the region above 190 cm^{-1}. It has been found that the nitrogen and argon matrices have different effects on the monomeric bands of water. Catalano and Milligan have observed seven sharp peaks (1654～1554 cm^{-1}) due to the bending vibration in the argon matrix but only one peak at 1600 cm^{-1} in the nitrogen matrix[3]. The observed fine structure in the argon matrix has been ascribed to overall rotations of the monomeric species in the argon matrix[**]. The rotations may not be unrestricted of course; however, they should be much less restricted in the argon matrix than in the nitrogen matrix. The present observation in the cesium iodide region is in accord with the conclusion drawn by Catalano and Milligan[2].

The author wishes to thank Professor K. S. Pitzer and Professor G. C. Pimentel of the University of California for their interest and

---

[*] In crystalline ice the ν_A and ν_C librations give rise to a band at 850 cm^{-1} (at −170°C). The two librations, however, have not been resolved from each other[7].

[**] It is interesting to note that NH_2 radical has been found to carry out almost free rotation in the argon matrix[8].

8) G. W. Robinson and M. McCarty, Jr., *J. Chem. Phys.* **30**, 999 (1959).

encouragement. The present work was partly supported by the American Petroleum Institute Research Project 50.

Institute for Protein Research
Osaka University
Kita-ku, Osaka