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Infrared spectra of T_2O ice

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There has been known two types of structure in ice–*I* at atmospheric pressure. One is the hexagonal ice and the other is the cubic ice I_c. A metastable ice I_v has also been known. It is well-known that there is no long-range order in the positions of hydrogen atoms in ice–*I*. Vibrational spectra of ice–*I* have been studied by many workers by both experimental observations[1–9] and interpretation.[10]

We may expect that T_2O ice is considerably different from ordinary ice, as found in electron bombarded ice.[11] On the other hand, T_2O ice may be unstable because of the high density of tritium, as found in β radiolysis of $[Co(en)_3]Cl_3 3T_2O$.[12] Fortunately we could report clear infrared spectra of T_2O ice.

T_2O was obtained from the reaction of 5 Ci T_2 with CuO at 320 °C. The infrared cell with a liquid N_2 reservoir was made of stainless steel with KRS-5 windows, which were stuck by using an In wire. The infrared spectrum for a film evaporated on a KRS-5 plate cooled by liquid N_2 was recorded on a JASCO IR-302 spectrometer in the region of 4000–330 cm^{-1}. The observed spectra are given in Fig. 1, where (a) and (b) are those observed directly ($t = 0$) and at 6 h ($t = 6$ h), respectively, after the formation of T_2O ice. The observed frequencies and their assignments are given in Table I.

The infrared spectrum was quite clear and changed little in 7 h, as shown in Fig. 1. This indicates that T_2O ice is stable and keeps the same structure. Although the mixing of hydrogen into T_2O ice was found from two bands at 3280 and 1429 cm^{-1}, the ratio of H to T is estimated to be less than 20% from being no band owing to H_2O. There was a sharp band at 2443 cm^{-1}, which is assigned to ν(O–D); D was included in a T_2 ampule.[13]

The change in frequencies and half bandwidths for ν(O–H) and ν(O–D) with time is given in Table II. The half bandwidth of ν(O–H) decreased from 150 to 107 cm^{-1} between $t = 0$ and 1 h, in ~10 minutes, the frequency being lowered by 6 cm^{-1}, whereas there was no further change for both the bands as well as other bands. The spectral change is ascribed to the phase transition from T_2O ice–I_v to I_c in good correspondence with the H system.[3,4,7,9,10] It is probable that the phase transition results from the high radiation dose (3.3×10^{20} eV/g in 10 min) as well as the formation of He and OT or OT^+ (5.9×10^{16} g in 10 min), by referring that the temperature of a KRS-5 plate was estimated to be 90 ± 4 K from the frequency of ν_3, 3512 ± 3 cm^{-1},[1–4] in H_2O ice-I_c in cold runs, though the actual temperature of a film is unknown. The O–H and O–D frequencies coincide almost with the decoupled ones in the D and H systems[6] in Table II, whereas the bandwidth in the T system is larger by ~4 times in ν(O–H) than that in the D system, which may indicate increase of an intrinsic width owing to decomposed species, trapped electrons, and *L* defects (at least 5.9×10^{16} g in 10 min).

TABLE I. Observed frequencies (cm^{-1}) and their assignments in T_2O ice at 90 K.

t/h		
0	6	Assignment
3472 sh	3464 sh	ν(O–T) + δ(HOT)
3291 s	3280 s	ν(O–H)
2446 m	2443 m	ν(O–D)
2174 sh	2175 sh	$\nu_1 + \nu_T$[a]
2104 s	2102 s	ν_3
2064 sh	2062 sh	$\nu(O–T)_{HTO}$
1988 ms	1985 ms	ν_1
1429 w	1429 w	δ(HOT)
1023 wm	1024 wm	$\delta(T_2O)$
800 m	798 m	HOT lib
541 s	541 s	T_2O lib

[a] ν_T: translational mode.

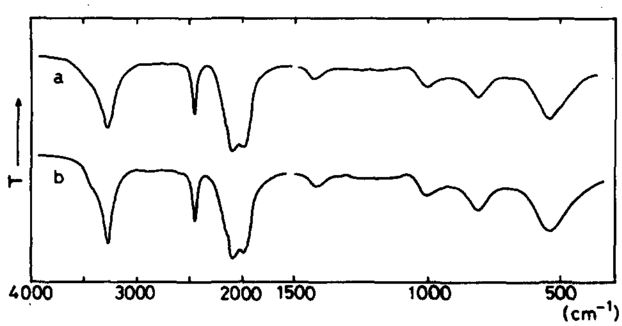

FIG. 1. Infrared spectra of T_2O ice at 90 K. (a) $t = 0$; (b) $t = 6$ h.

TABLE II. Variation of frequencies and bandwidths (cm^{-1}) with time.[a]

t/h	0	1	2	6	H system[b]
ν(O–H)	3291 (150)	3285 (107)	3283 (106)	3280 (110)	3279 (30)
ν(O–D)	2446 (38)	2447 (37)	2445 (35)	2443 (38)	2423 (20)

[a] Bandwidth in parentheses.
[b] From Raman spectra for 3 mol % HDO diluted water at 123 K (Ref. 4).

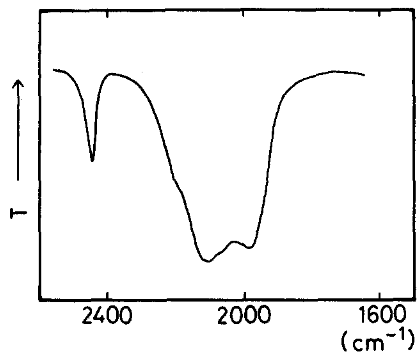

FIG. 2. Infrared spectrum in the region of O–T stretchings of T_2O ice-I_c at $t = 0$.

The infrared spectrum in the region of O–T stretchings of T_2O ice-I_c at $t = 0$ is given in Fig. 2. Two bands at 2104 and 1988 cm^{-1} are assigned to ν_3 and ν_1, respectively. The spectrum seems not so resolved as expected.[3] One of the reasons is overlapping with the O–T stretching of HTO, which is expected to be lower than ν_3.[3] A shoulder at 2064 cm^{-1} may be, thus, assigned to the O–T stretching. On the other hand, the main reason is probably that the bandwidths are broad in themselves, as described above.

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