OBSERVATION OF INFRARED ABSORPTION SPECTRA OF MOLECULAR IONS, H^{*}₃ AND HN^{*}₂, BY FTIR SPECTROSCOPY

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The infrared absorption spectra of the molecular ions H_3^+ and HN_2^+ were measured by using the Fourier-transform infrared method and a hollow-cathode discharge cell. From the analysis of the relative intensities and the linewidths of the absorption lines, these ions in the ground vibrational states were found to be well thermalized in the cell. The band center of the ν_1 mode of HN_2^+ has been determined to be 3233.9608(2) cm⁻¹ which is slightly higher than the literature value.

1. Introduction

Since the observation of the infrared absorption spectrum of H₃⁺ by Oka [1], the infrared spectra of various molecular ions have been studied mainly by the use of laser spectroscopic techniques. Although the observation of the infrared spectrum of ion by Fourier-transform infrared (FTIR) spectroscopy was initiated by Brault and Davis [2], only a few molecular ions have been studied by this method [3-5]. In addition, they were observed as emission spectra, and no observation of absorption FTIR spectrum has been reported so far. This is due to the fact that the sensitivity of the FTIR method is one or two orders of magnitude lower than that of laser spectroscopy, and that only a single noise of the electric discharge can spoil the whole spectrum. Nevertheless, it still seems desirable to observe the absorption spectrum of short-lived species, such as molecular ions with FTIR spectroscopy, since the spectrum of a wide frequency range can be recorded easily, and more reliable values of the frequencies and the relative intensities of absorption lines can be obtained.

In the authors' laboratory, an FTIR spectrometer with a small White-type long-path cell, which can be evacuated rapidly, has been used to detect short-lived species [6]. This system was applied to the detection of the infrared absorption spectra of molecular ions of H_3^+ and HN_2^+ . These ions, which are of interest because of their important roles in astrophysics, have been investigated frequently including the studies of the ion-molecular reaction dynamics [7]. In the present work, the infrared absorption spectra of H_3^+ and HN_2^+ have been measured for the first time with the FTIR method by using a hallow-cathode discharge cell, and thereby the temperatures of the ground states of these ions have been determined, as well as the band center of the ν_1 mode of HN_2^+ has been refined.

2. Experimental

Fig. 1 shows the schematic diagram of the experimental system. A stainless steel hollow cathode 400 mm in length and 65 mm in diameter and a brass anode 22 mm in diameter were installed in a glass





White-type long-path cell. The cathode was cooled by water from the outside of the cell. H_3^+ and HN_2^+ were generated through a dc discharge inside the absorption cell. For the formation of H_3^+ pure hydrogen was used, and a small amount of nitrogen was added to hydrogen gas for the formation of HN_2^+ . The absorption signal of H_3^+ could be observed when the pressure of H_2 was higher than 50 Pa and the discharge current was larger than 200 mA. The discharge was stable enough to accumulate the interferogram for several hours when the pressure of H_2 was 100 Pa and the discharge current was 300 mA.

The infrared absorption spectra were measured with a BOMEM DA3.36 FTIR spectrometer using an InSb detector and a CaF₂ beam splitter. The range of spectrum was limited to about 400 cm⁻¹ when the resolution of 0.005 cm⁻¹ was used because of the memory size of the computer system. The dimensions of the White-type long-path cell was 500 mm in length and 70 mm in diameter, and the effective optical path length was about 10 m. The cell was evacuated by both a rotary pump and a roots vacuum pump (Edward 40 and EH2500).

3. Results and discussion

Fig. 2 shows a part of the infrared absorption spectrum of H_3^+ generated by a dc discharge in 100 Pa of H_2 with a current of 300 mA. The resolution was 0.005 cm⁻¹ and the interferogram was accumulated



Fig. 2. Part of the absorption spectrum of H_3^+ ion. The resolution was 0.005 cm⁻¹ and the interferogram was accumulated for 92 times.

92 times. The absorption intensity of the transitions of H_3^+ was not strongly affected by the discharge condition. The absorption of H_3^+ could be observed when the pressure of H_2 was higher than 50 Pa, and the discharge current was larger than 200 mA. One of the absorption lines of the Brackett series of the H atom (2467.744 cm⁻¹, $n=5 \leftarrow 4$) was also observed in the same spectrum, but its intensity was more sensitive to discharge conditions than that of H_3^+ .

Each observed line shape of H_1^+ was fitted to the Gaussian profile to determine the line position, the linewidth, and the integrated intensity. Table 1 shows the parameters thus determined for the absorption lines which lie between 2400 and 2800 cm^{-1} and were strong enough to determine the integrated line intensities. The observed frequencies agreed well with the literature values [8] with a mean deviation of less than 0.002 cm^{-1} . The number density of each rotational state of H_3^+ was estimated by using the transition dipole moment for each transition calculated by Miller and Tennyson [9]. The plot of $\log(N_{\rm ion}/g_{\rm spin})$ versus the ground-state energy gives a straight line (fig. 3) from which the rotational temperature $T_{\rm rot}$ has been determined to be 386(20) K. From these data, the total number density of H_3^+ was estimated to be 5×10^{10} cm⁻³ in the present experimental conditions.

The translational temperature $T_{\rm tr}$ was also determined from the Doppler linewidth. Since the present resolution of 0.005 cm⁻¹ was not negligibly small compared with the Doppler width (0.02 cm⁻¹), the true linewidth was estimated from the observed linewidth by a deconvolution technique. The observed linewidth was found to be about 3% larger than the true one under the present experimental conditions. The ratio of the Doppler width to the transition frequency was determined to be

 $\Delta v_{1/2} / v = 0.781 \times 10^{-5}$.

This value leads to the translational temperature of $T_{\rm tr} = 360$ K. The error limit of $T_{\rm tr}$ was estimated to be about 10%. Since $T_{\rm tr}(360$ K) and $T_{\rm rot}(386$ K) are almost the same, the ground state of H₃⁺ ion seems to have been thermalized completely. This result is consistent with that of Amano [7].

Fig. 4 shows the infrared absorption spectrum of HN_2^+ observed with the resolution of 0.008 cm⁻¹ and

Assignment	Frequency *) (cm^{-1})	Intensity ^{a)} (10^{-3}cm^{-1})	$\Delta \nu_{1/2}^{a}$ (cm ⁻¹)	№ ^{ъ)} (10 ⁹ ст ⁻³)	
01+111	2457.2897	0.183(59)	0.0228(38)	6.97	
32_132	2503.3486	0.204(46)	0.0194(23)	2.32	
31_131	2508.1341	0.268(35)	0.0215(15)	1.69	
30_130	2509.0776	0.485(73)	0.0190(15)	2.68	
21_121	2518.2102	0.390(40)	0.0194(11)	4.46	
10_10	2529.7247	1.155(56)	0.0200(5)	14.46	
11+111	2545.4170	0.399(55)	0.0224(17)	9.80	
33+133	2561.4958	0.353(56)	0.0202(17)	7.32	
$21_{-1}11$	2591.4408	0.325(50)	0.0237(20)	6.90	
20_110	2725.8987	1.419(82)	0.0266(7)	16.14	
$21_{\pm 1}11$	2726.2186	0.422(51)	0.0227(15)	7.86	
32_122	2762.0692	0.532(50)	0.0211(11)	5.23	

Table 1	
Observed frequencies and intensities of H ₃ ⁺	$(in cm^{-1})$

^{a)} These parameters were determined by the fitting of the observed line to a Gaussian profile. The values in the parentheses are the standard deviation of the fits.

^{b)} Number density of H_3^+ in each rotational state.



Fig. 3. Plot of $\log(N/g)$ versus E_g of the H₃⁺ ion. The rotational temperature of the H₃⁺ was determined to be 386(20) K from the slope of the line.

by accumulating the interferogram for 208 times. HN_2^+ was generated from the reaction

$$H_3^+ + N_2 \rightarrow H_2 + HN_2^+$$
,

induced by the discharge in the mixture of 100 Pa of H_2 and 6 Pa of N_2 . When the partial pressure of N_2 was increased, the intensity of HN_2^+ became weak, and the discharge became rather unstable. In the same spectrum, the NH₃ and NH radicals were also identified.

Table 2 shows the frequencies and the intensities of the observed absorption lines of HN_2^+ determined by fitting the observed line shape to the Gaussian



Fig. 4. Infrared absorption spectrum of HN_2^+ . Resolution was 0.008 cm⁻¹, and the interferogram was accumulated for 208 times.

profile. Although the observed line shape was not strictly a Gaussian profile because the resolution of the spectrometer (0.008 cm^{-1}) was about the same as the Doppler width, the fit was generally good. The error due to this effect was estimated by a numerical calculation to be less than a few percent when the absorption of the peak was less than 2%. The intensity distribution of the vibration-rotation lines was calculated with the following equations:

$$S_{R(J)} = S_0(J+1) \exp(-E_g/kT_{rot}),$$

$$S_{P(J)} = S_0 J \exp(-E_g/kT_{rot}).$$

A least-squares fit showed that $S_0 = 3.40(9) \times 10^{-5}$ cm⁻¹ and $T_{rot} = 408(12)$ K. T_{rot} of HN₂⁺ was found to agree well with T_{rot} and T_{trans} of H₃⁺, which im-

Table 2	
Observed frequencies and intensities of the v, band of HN	V_{i}^{+} (in cm ⁻¹)

J	R(J)				P(J)			
	frequency		intensity ")		frequency		intensity *)	
	V	o-c ^{b)}	S	0-c ^c	ν	0-c ^{b)}	s	0-c °)
0	3237,0440 d)	5						
1	3240.1009 4)	-1			3230.8513 ^d)	-16		
2	3243.1323	-8	9	-1	3227.7207	9	6	0
3	3246.1389	-9	14	1	3224.5613	4	11	1
4	3249,1211	1	16	1	3221.3788	2	14	2
5	3252.0769	2	16	-2	3218.1704	-1	13	-1
6	3255.0068	1	19	0	3214.9381	5	17	1
7	3257.9110	-1	19	-1	3211.6799	-1	16	-2
8	3260.7899	2	19	-1	3208.3976	0	18	-1
9	3263,6424	-1	21	0	3205.0906	0	20	1
10	3266.4695	2	22	1	3201.7595	5	17	-2
11	3269,2703	0	19	-1	3198.4031	1	19	1
12	3272.0451	-1	22	3	3195.0226	1	17	0
13	3274.7938	-2	17	-1	3191.6180	3	14	-2
14	3277.5169	2	18	1	3188.1887	1	17	1
15	3280.2130	-2	15	1	3184.7344	-9	13	-1
16	3282.8841	8	14	0	3181.2577	-3	12	0
17	3285.5268	-4	11	-1	3177.7557	-8	9	-2
18	3288.1456	10	11	1	3174.2317	6	11	2
19	3290.7352	-3	6	-3	3170.6828	10	7	-1
20	3293.2979	-19	9	2	3167.1078	-10	7	0
21	3295.8389	12	6	0	3163.5123	4	8	2
22	3298.3483 ^{d)}	-5			3159.8888 ^{d)}	- 26		
23	3300.8331 ^d	-1			3156.2485 ^d)	12		
24	3303.2896 ^d)	-12			3152.5828 ^d)	31		

*) Integrated intensity in 10^{-6} cm⁻¹. b) $(\nu_{obs} - \nu_{calc}) \times 10^4$ cm⁻¹. c) $(S_{obs} - S_{calc}) \times 10^6$ cm⁻¹.

^{d)} The S/N ratios of these lines were not very good, so that the integrated intensities of these lines were not estimated. The weights of these lines were set to 1/16 of the other lines in the least-squares fit.

plies that the molecular ions in the hollow cathode are well thermalized. The integrated band intensity was calculated from the above parameters to be 6.4×10^{-3} cm⁻¹. With the value of band intensity predicted by an MO calculation [10], the density of the HN₂⁺ ion was estimated to be 6×10^{10} cm⁻³, which was about the same as that of H₃⁺ generated by the dc discharge through pure H₂ gas.

The infrared spectra of HN_2^+ have been studied extensively by many investigators. Owrutsky and coworkers [11] have already made a complete analysis of all vibrational modes of HN_2^+ . The observed frequency values of the present work, however, are slightly higher than those in ref. [11]. The reliability of the present data was confirmed by the comparison of the transition frequencies of the ν_1 band of NH₃ observed in the same spectral region with the literature values [12] for which a strict frequency determination had been made. From this comparison, the error of the absolute frequency of the present work was estimated to be less than 0.002 cm⁻¹. Therefore, the molecular constants of the ν_1 band have been re-determined using the present data together with the reported transition frequencies in the millimeter and sub-millimeter wave regions [13–16]. The results are given in table 3 together with those obtained by Owrutsky et al. [11]. The observed frequencies are reproduced well by these constants, and the mean deviation of the calculated frequencies is much smaller than theirs. The refined band center of

Table 3	
Molecular constants of HN ₂ ⁺	$(in cm^{-1})$

	Present work	Ref. [11] *)
<i>v</i> ₀	3233.9608(2)	3233.9530(8)
B ₁	1.541369(22)	1.541357(30)
D_1	0.000002912(53)	0.000002901(23)
$\dot{B_0}$	1.5539707(16)	1.553971(33)
D_0	0.000002926(34)	0.000002928(25)

^{a)} In ref. [11] are two typographical errors which are corrected in this table.

 v_1 is 3233.9608 cm⁻¹ which is higher than that of ref. [11] by 0.008 cm⁻¹.

In this experiment, the FTIR absorption spectra of two molecular ions were successfully observed, and reliable intensities and frequencies of the vibrationrotation lines were obtained. This study clearly showed the usefulness of the FTIR absorption method for the investigations of short-lived species, such as molecular ions.

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