Detection of the Hydronium Ion (H₃O⁺) by High-Resolution Infrared Spectroscopy

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(Received 8 June 1983)

The first high-resolution measurement of the ν_3 vibration (doubly degenerate asymmetric stretch) of the hydronium ion (H₃O⁺) is reported. An analysis of sixty transitions in the symmetric and antisymmetric inversion states yields effective band origins of 3530.165(55) and 3513.840(47) cm^{-1}, respectively.

The structure and bonding properties of hydrated proton complexes control the dynamics of proton transfer in aqueous solutions, and it is the hydronium ion (H₃O⁺) that is the fundamental entity in the hydrated proton series $H_3O^+ \cdot (H_2O)_n$. Its structure, thermodynamic properties, and vibrational frequencies have been the subjects of numerous theoretical[1-3] and experimental studies in condensed phases,[3] and its thermochemistry and kinetics have been investigated in the gas phase.[3] In an important experiment done in 1977, Schwarz[4] measured broad-band vibrational spectra of the hydronium ion and its associated hydrates with n as large as six by pulsed radiolysis of water vapor contained in argon at atmospheric pressure. No other gas-phase spectrscopic investigations of this species have been carried out until the present study. Using the technique of velocity-modulated absorption spectroscopy,[5,6] we have observed and measured the ν_3 vibration-rotation band of H₃O⁺ with high resolution near 2.8 μm in an ac glow discharge. Because H₂O is an extremely strong absorber near 2.8 μm, and is at least 10^4 times more abundant than H₃O⁺ in the discharges used here, the selectivity of the velocity-modulation technique for ionic absorptions was essential to the success of this experiment.

The experimental arrangement is the same as that employed previously in studies[5,6] of HCO⁺ and HNN⁺. The ν_3 spectrum of H₃O⁺ was observed both in liquid nitrogen (LN₂)-cooled (Fig. 1) and in air-cooled room-temperature (RT) 1–3-kHz discharges through flowing mixtures of hydrogen and oxygen with a H₂/O₂ ratio of ~3/1 and total pressures of ~1.3 Torr, in which H₃O⁺ is expected to be an abundant ion.[7] The discharge current was approximately 30 mA in all cases. The region from 3310–3655 cm^{-1} was scanned by tuning the color-center laser in mode-hop increments of 300 MHz, determined by the longitudinal mode spacing of the cavity. Frequencies were measured with an accuracy of 1 part in 10^6 by av-

eraging the frequencies of the up and down lobes of the first-derivative signal using a Burleigh wavemeter. With LN₂ cooling approximately 90 lines were measured in the region from 3435 to 3655 cm^{-1}. Although the signal-to-noise ratio was independent of the temperature of the cell wall, ~150 additional lines were measured at RT, many of which could not be assigned to H₃O⁺. The band origin for the ν_1 vibration (symmetric stretch) is predicted to lie 110 cm^{-1} below that of the ν_3 band, and to be 13 times weaker.[1] As a result of the calculated inversion splittings (72 cm^{-1} in the ground state and 94 cm^{-1} in the $\nu_1 = 1$ state[2]), one inversion component of the ν_1 band could overlap with the ν_3 band. The lines observed to the red of the ν_3 band at RT were of approximately the same intensity as those assigned to ν_3 and could not reasonably be assigned
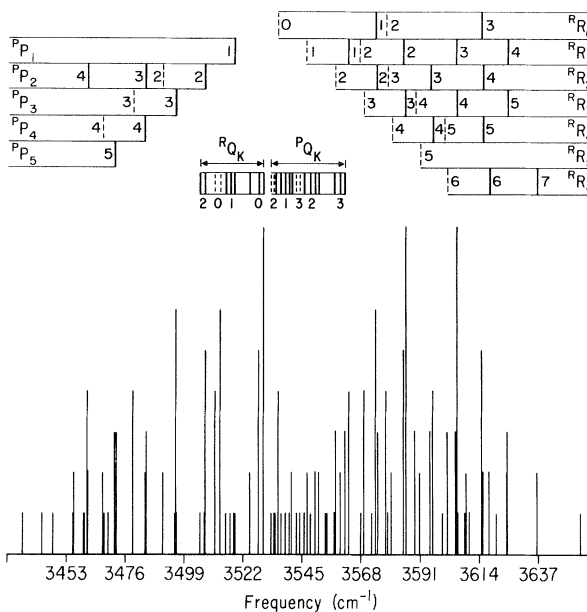

FIG. 1. Reconstructed spectrum of the ν_3 band of H₃O⁺ measured with LN₂ cooling. In assignment, dashed lines correspond to asymmetric inversion band, solid lines to symmetric.

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to ν_1, particularly because no such band was observed at LN_2 temperatures. These additional lines are most likely due to hydrated forms of the hydronium ion.[4]

The assignment of the observed spectrum to H_3O^+ is based on isotope substitution experiments and on a spectroscopic analysis of the lines measured at LN_2 temperatures. The decrease in signal amplitude upon the addition of deuterium to the discharge was quantitatively measured with use of D_2/H_2 ratios of 1/9, 2/8, and 3/7. When the transitions were measured with $1f$ detection, i.e., detecting at the ac modulation frequency, these results indicated 3.4 ± 0.2 hydrogens per molecule. (All uncertainties are 90% confidence intervals.) However, when the same experiment was done with $2f$ detection, the results were 2.8 ± 0.3 hydrogens. The larger value for the $1f$ result is explained by the fact that the addition of deuterium to the discharge changes the electric field in the discharge and reduces the mobility of the ions because of an increase in the reduced mass of the ion-neutral collision partners. These effects cause an additional decrease in the signal amplitude when ion velocity modulation is used, independent of the statistical decrease due to the deuteration of the molecule. Such effects became more apparent at higher concentrations of D_2. Correcting the $1f$ results for the increase in reduced mass upon the addition of D_2 to the discharge, we determine that the spectral carrier contains 3.2 ± 0.2 hydrogens. With $2f$ detection one is sensitive to modulations in the concentration of the species, and hence the signal amplitude is much less dependent on changes in ion mobility. Additional systematic uncertainties in the isotope substitution experiments arise, however, since the plasma density and electric field depend on the discharge composition. We were unable to measure changes in these parameters as a function of D_2 pressure.

As mentioned above, the H_3O^+ ν_3 spectrum could be observed at RT in H_2O/H_2 discharges, allowing us to generate the ^{18}O-substituted species using $H_2^{18}O$ as a precursor. The substitution of $H_2^{18}O$ for $H_2^{16}O$ affects the discharge parameters much less than in the D_2/H_2 case, and hence the $1f$ results agree well with the $2f$ results. With a $H_2^{16}O/H_2^{18}O$ ratio of 1/1, an average signal decrease of $(50.4 \pm 1.2)\%$ was observed, indicating a molecular species containing only one oxygen. Twenty-eight lines due to the ^{18}O-containing species were measured. Although the complete $H_3^{18}O^+$ spectrum was not recorded, an isotope

shift of -13.5 to -15 cm^{-1} relative to $H_3^{16}O^+$ was determined from the recognizable pattern of the ten strongest lines. This isotope shift agrees well with the theoretical calculations.[2]

The ν_3 vibrational mode of H_3O^+ is the doubly degenerate asymmetric stretch. Excitation of this vibration results in a change in the dipole moment perpendicular to the symmetry axis of the molecule and thus the spectrum exhibits the features of a perpendicular-type band. Because H_3O^+, like NH_3, is pyramidal, the spectrum possesses features attributable to the inversion doubling of all states. The molecular constants presented in Table I were determined by separate least-squares fits of the antisymmetric → antisymmetric (a-a) and symmetric → symmetric (s-s) inversion components by standard formulas for the P, R, and Q branches as a function of K, and J, $J+1$, and $J(J+1)$, respectively.[8] A total of 38 lines were used for the s-s band and 22 for the a-a. The remaining weak lines in the spectrum have not as yet been assigned. Because of the limited number of lines observed in each band, the higher-order constants were not well determined and are not reported here. The most prominent lines belong to $^kQ_0(J)$ and to $^kP_K(J = K)$ and $^rR_K(J = K)$ series. All assigned P and R lines were attributed to transitions in which $\Delta J = \Delta K$. The highest J and K levels observed were $J, K = 6$, and the rotational distribution peaked at $\sim J = 3$, indicating a rotational temperature of ~ 200 K, as observed in our previous experiments.[5,6] Because only the ν_3 band has been observed here, it is not possible to determine C' independently, but only the combination $C'(1 - \zeta)$. Moreover, only an effective vibrational frequency, $\nu_{eff} = \nu_0 + C'(1 - 2\zeta) - B'$, can be determined. However, by using the theoretical value for $C'' - B''$ reported by Bunker and co-workers[2] and our experimental values for B' and B'', we can obtain values for C'' and C' and therefore can approximate the molecular geometry (Table I).

In perpendicular bands the frequency separation of transitions from each inversion component is equal to the difference in the inversion splitting in the excited and ground states. We observe (Table I) a $16.4(1)$-cm^{-1} separation in these inversion components. For the $K = 0$ subband the lines do not appear as inversion doublets, but are alternately red and blue shifted. The observed positions of these lines indicate that the s-s band is at the higher frequency; therefore the inversion splitting in the excited state is less than that in the ground state. This is the case

TABLE I. Molecular constants (inverse centimeters) for H_3O^+ derived from analysis of the ν_3 band. All uncertainties correspond to one standard deviation.

	Present work	Colvin et al.	Bunker et al.
Symmetric (s)			
ν_{eff} [a]	3530.165(55)	3512	3666
B''	11.23(11)	$B_e = 11.605$	11.14
B'	11.00(11)		
$C'(1-\zeta)$	5.60(11)		
$(C'-B')-(C''-B'')$	0.199(8)		
C'' [b]	6.14(11)	$C_e = 6.396$	6.05
C'	6.11(11)		
Antisymmetric (a)			
ν_{eff}	3513.840(47)		3660
B''	10.957(36)		
B'	10.788(36)		
$C'(1-\zeta)$	5.693(36)		
$(C'-B')-(C''-B'')$	0.132(7)		
C'' [c]	6.177(36)		6.16
C'	6.140(36)		
r_{OH} (Å) [b]	0.979(6)	0.962	0.978
$\angle$ HOH (deg)	114.91(45)	114.1	111.6

[a] $\nu_{eff} = \nu_0 + C'(1-2\zeta)-B'$. Schwarz (Ref. 4) reports 3490 cm^{-1}.
[b] Structural parameters are average values for the lowest (s) vibronic state.
[c] C'' and C' calculated with use of theoretical $C''-B''$ value from Bunker and co-workers (Ref. 2) and the experimental B'' and B' values.

for NH_3, and is predicted[2] for H_3O^+. The intensity of the a-a band is expected to be less than that of the s-s band by an amount corresponding to the splitting in the ground state and the temperature of the discharge. The transitions originating in the ground-state a level were $\sim\frac{2}{3}$ as strong as those originating in the s level. This is consistent with a ground-state inversion splitting of ~ 72 cm^{-1} as predicted by Bunker and co-workers and an inversion temperature of ~ 200 K, which appears to be equilibrated with the observed T_{rot}.

The analysis of the ν_3 vibration-rotation band of H_3O^+ presented here is preliminary; a complete determination of the molecular parameters will require measurement of the ν_1 band of H_3O^+, the a' and a'' bands of H_2DO^+, the a' band of HD_2O^+, and the ν_1 and ν_3 bands of $H_3^{18}O^+$, all of which are predicted to lie near 2.8 μm.[1,2] Such measurements will allow the determination of an accurate substitution (R_s) structure for hydronium. The study of H_3O^+ reported here, as well as our recent detection of the ammonium ion (NH_4^+),[9] illustrates the power and simplicity of the velocity modulation technique for studying polyatomic

molecular ions generated in chemically complicated environments.

Finally, we find it most encouraging to note the excellent agreement between our results and the ab initio predictions of Colvin et al.[1] Such reliable calculations are of considerable importance in searching for and assigning spectra of polyatomic molecules like H_3O^+.

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