Observation of the ν_2 ($1^- \leftarrow 0^+$) inversion mode band in H_3O^+ by high resolution infrared spectroscopy[a]

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The potential energy barrier to inversion of the oxonium ion H_3O^+ has been a subject of interest for many years.[1-10] We report the first observation of the high resolution gas phase ν_2 ($1^- \leftarrow 0^+$) band in absorption by diode laser spectroscopy, an initial step in determining the barrier. In Fig. 1 we show the energy levels and potential energy associated with the ν_2 inversion mode, analogous to the classical case in ammonia. Measurement of the three indicated infrared bands gives the 0^-–0^+ inversion splitting from which the barrier can be determined.[11]

Infrared (and NMR) spectra of H_3O^+ have been observed for over 30 years[1,12-18] in crystals and solution, and our work supports the earlier ν_2 assignments in the 1000–1200 cm^{-1} region. The ν_3 stretching mode has been observed in the gas phase by Schwarz[19] in low resolution, pulsed radiolysis experiments. Recently, Saykally and coworkers[20] observed this band at high resolution using the ac discharge velocity modulation technique. The importance of H_3O^+ in the chemistry and structure of liquids is well established[21,22] especially with regard to hydrogen bonding in biological systems. The H_3O^+ ion is also of central importance in the chemistry of ionized gases, e.g., in laboratory discharges and flames,[23,24] in the upper atmosphere,[25] in comets,[26] and in the interstellar medium.[27] The ν_2 frequencies reported here can be used to observe H_3O^+ in these environments, e.g., by infrared astronomy.

The vibration-rotation absorption spectral lines were observed in a 2 kHz ac glow discharge ($\sim$400 W) through a 3:1 mixture of H_2/H_2O gas at 2 Torr that was pumped through a 150 cm water cooled Pyrex cell of 0.9 cm i.d., much as in Ref. 20. The ion mobility of H_3O^+ in the gas mixture and the axial electric field ($\sim$20–30 V/cm) were sufficient to observe $1f$ velocity modulated absorption spectra.

Two laser analytics mesa-stripe geometry tunable diode lasers were used for infrared sources. Three Q branch transitions are shown in Fig. 2 with typical signal to noise ratios and linewidths. The central feature represents a fractional infrared absorption of 0.08%, which is consistent with an ion density of $\sim 5 \times 10^{10}$ cm^{-3}, a 150 cm path length, and an absorption cross section of 0.1 Å^2 ($\mu \sim 0.4$ D[28] and $T = 600$ K). Further details on drift velocity effects in infrared spectra and on velocity modulation spectroscopy are available in Refs. 29 and 30. Three key elements in the success of this experiment were the improved performance of stripe geometry lasers,[31] the sensitivity of velocity modulation techniques,[30] and the accurate theoretical prediction of the spectrum.[32]

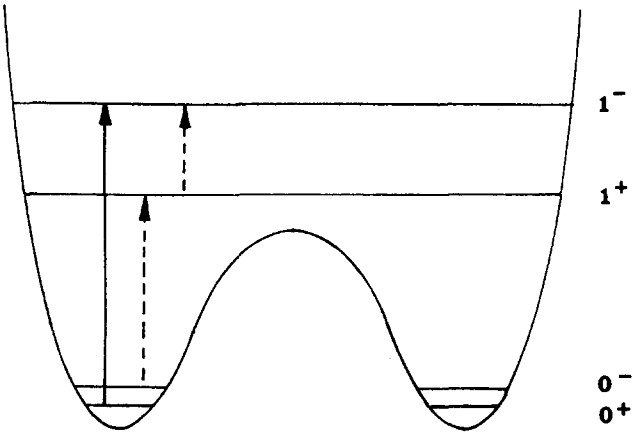

FIG. 1. Sketch of the double well potential for H_3O^+ showing the observed band (solid line) and other IR bands (dashed lines).

The observed transition frequencies (with a present, but improvable accuracy of $\pm$ 0.005 cm^{-1}) are listed in Table I. They fit reasonably well (average deviation = 0.02 cm^{-1}) to the usual parallel band symmetric top expression,[33] with the constants also given in the tabulation. The obviously missing lines are due to gaps in the diodes' frequency coverage. The agreement with the purely *ab initio* calculations[32] of Bunker, Kraemer, and Spirko is striking, but is also consistent with other such successes of high quality *ab initio* calculations on ions.[34-37] The ground state rotational B value is in good

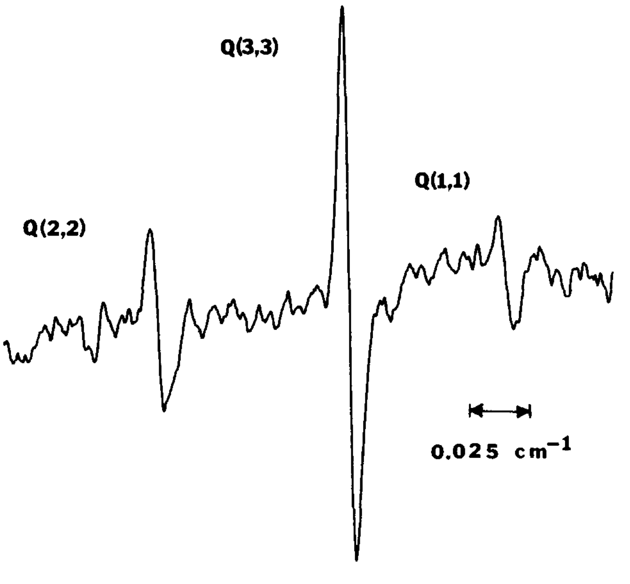

FIG. 2. Q branch transitions of ν_2 ($1^- \leftarrow 0^+$) H_3O^+. Time constant of 1 s, integration of 10 s over full linewidth.

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TABLE I. Line positions and molecular constants (cm^{-1}).

$P(5,0)$	831.709	$Q(11,11)$	964.474
$P(5,2)$	834.151	$Q(12,12)$	967.158
$P(4,1)$	858.779	$Q(2,1)$	951.779
$P(4,3)$	864.008	$Q(3,2)$	950.499
$P(3,1)$	884.365	$Q(5,4)$	948.705
$P(3,2)$	886.359	$Q(6,5)$	948.215
$Q(1,1)$	953.975	$Q(7,6)$	947.961
$Q(2,2)$	953.806	$Q(8,7)$	947.981
$Q(3,3)$	953.897	$Q(9,8)$	948.239
$Q(4,4)$	954.254	$Q(10,9)$	948.766
$Q(5,5)$	954.867	$Q(13,12)$	951.764
$Q(6,6)$	955.752	$R(1,0)$	996.064
$Q(7,7)$	956.922	$R(2,2)$	1017.951
$Q(8,8)$	958.354	$R(3,0)$	1033.281
$Q(9,9)$	960.083	$R(3,1)$	1033.963
$Q(10,10)$	962.120	$R(3,3)$	1039.391

	Observed	Predicted[a]
ν_0	954.417(14)	992
B_1	10.690(4)	10.66
B_0	11.253(4)	11.14
$(C_1\text{-}B_1) - (C_0\text{-}B_0)$	0.694(15)	0.67
$D_{1,J}$[a]	1.8(2)	7.8
$D_{0,J}$	13(1)	11.0
$D_{1,JK}$	− 1.9(1)	− 10.7
$D_{0,JK}$	− 30(4)	− 22.5
$D_{1,K} - D_{0,K}$	− 20(10)	− 9.2

[a] Centrifugal distortion constants in units of 10^{-4} cm^{-1}.
[b] Reference 32.

agreement with the result of 11.23 ± 0.11 cm^{-1} from the ν_3 band spectrum.[20]

Future laboratory experiments will focus upon the other transitions in Fig. 1, as well as further refinement of the present band and the usual isotopic substitution work for a molecular structure. Also, this observation of 10 μm wavelength ion transitions opens up the possibility of subdoppler saturation spectroscopy of ions employing the ultrahigh spectral purity infrared sources which operate in this region.[38]

Note added in proof: Just recently Botschwina, Rosnus, and Reinsch[39] have theoretically predicted the present μ_2 band origin to be at 961 cm^{-1}, which is in excellent agreement with our results.

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