

The ν_2 $1^- \leftarrow 0^+$ Band of $\text{H}_3^{18}\text{O}^+$

The high-resolution infrared spectrum of the H_3O^+ molecular ion has been studied quite extensively since the first high-resolution spectroscopic study of the ν_3 band of H_3O^+ by Begemann *et al.* (1). Spectroscopically, much interest has been focused on the ν_2 vibration of this ion. Being isoelectronic with the ammonia molecule, H_3O^+ has a pyramidal equilibrium structure, and the potential function for the out-of-plane bending mode has a lower barrier of inversion. The vibrational energy levels associated with the ν_2 mode are split by the inversion tunneling through the barrier. The $1^- \leftarrow 0^+$ band of the ν_2 vibration-inversion was first reported in 1984 (2) in the 10- μm region. Subsequently other workers have reported the experimental measurement of the other bands, and the ground state inversion splitting has been accurately determined (3); this led to the direct measurement of the $0^- \leftarrow 0^+$ band in the submillimeter-wave region (4, 5). The ν_2 band of the isotopically substituted D_3O^+ was also studied by Sears *et al.* (6) and provided equilibrium structures and vibrational potential functions of H_3O^+ and D_3O^+ .

In this paper, we report our experimental measurement of the $1^- \leftarrow 0^+$ band of $\text{H}_3^{18}\text{O}^+$ around the 10- μm region. This limited ^{18}O isotopic study allows us to determine the isotope shift in the band origin; this result may be useful in characterizing the potential function, and to possibly further refine the equilibrium structure and force constants of H_3O^+ .

The experimental setup is similar to that we reported earlier (2). H_3O^+ was produced in a water-cooled ac glow discharge cell with a gas pressure of 400 mTorr of a 50/50 mixture of $^{18}\text{O}/^{16}\text{O}$ water and about 1 Torr of H_2 . The velocity modulation technique of Gudeman *et al.* (7) was used to discriminate the ion signals from the stronger neutral absorptions and to increase the signal-to-noise ratio. Sixteen measured lines of R- and Q-branch transitions are listed in Table I. Due to the limited coverage of the diode lasers,

TABLE I
Observed Line Positions in the $1^- \leftarrow 0^+$ Band of $\text{H}_3^{18}\text{O}^+$ (cm^{-1})

Transition	Frequency	Obs. - Calc.
R (4,3)	1044.462	+0.001
R (3,3)	1027.608	-0.001
R (3,1)	1022.208	+0.002
R (3,0)	1021.546	-0.002
R (2,1)	1004.179	-0.001
R (1,1)	985.060	-0.003
R (1,0)	984.381	+0.004
Q (12,12)	955.144	+0.001
Q (11,11)	952.524	-0.002
Q (9,9)	948.252	+0.001
Q (7,7)	945.169	+0.000
Q (6,6)	944.647	-0.001
Q (4,4)	942.604	+0.000
Q (3,3)	942.270	+0.001
Q (2,2)	942.191	+0.004
Q (1,1)	942.349	-0.005

TABLE II

The Molecular Constants in the $1^- \leftarrow 0^+$ Band of $\text{H}_3^{18}\text{O}^+$ (cm^{-1})

Quantity	Value	Stand. dev.
ν_0	942.7702	7.1×10^{-3}
$(C' - B') - (C'' - B'')$	0.6639	8.4×10^{-3}
B'	10.6866	3.5×10^{-3}
B''	11.2274	3.4×10^{-3}
D'_j	1.8×10^{-4}	0.6×10^{-4}
D''_j	3.4×10^{-4}	1.0×10^{-4}
D'_{JK}	-4.3×10^{-4}	1.8×10^{-4}
D''_{JK}	-7.8×10^{-4}	2.5×10^{-4}
$D'_K - D''_K$	-1.9×10^{-4}	0.3×10^{-4}

other transitions were not observed. The frequencies of the transitions were calibrated by the FTIR spectra of SO_2 and D_2CO gas kindly provided by J. W. C. Johns of the Herzberg Institute of Astrophysics. The spectrum was fitted to the energy expression of the parallel band of the symmetric top molecule using the linear least-squares method; molecular constants thus obtained are listed in Table II. The isotope shift from the H_3O^+ band origin of 954.4001 cm^{-1} is $11.6299 \pm 0.007 \text{ cm}^{-1}$, which is very close to the theoretical prediction by Bunker *et al.* (8).

ACKNOWLEDGMENT

This work is supported by National Science Foundation Grant NSF PHY 8707025.

REFERENCES

1. M. H. BEGEMANN, C. S. GUEDEMAN, J. PFAFF, AND R. J. SAYKALLY, *Phys. Rev. Lett.* **51**, 554-557 (1983).
2. N. N. HAESE AND T. OKA, *J. Chem. Phys.* **80**, 572-573 (1984).
3. D.-J. LIU, T. OKA, AND T. J. SEARS, *J. Chem. Phys.* **84**, 1312-1316 (1986).
4. G. M. PLUMMER, E. HERBST, AND F. C. DE LUCIA, *J. Chem. Phys.* **83**, 1428-1429 (1985).
5. M. BOGEY, C. DEMUYNCK, M. DENIS, AND J. L. DESTOMBES, *Astron. Astrophys.* **148**, L11-L13 (1985).
6. T. J. SEARS, P. R. BUNKER, P. B. DAVIES, S. A. JOHNSON, AND V. ŠPIRKO, *J. Chem. Phys.* **83**, 2676-2685 (1985).
7. C. S. GUEDEMAN, M. H. BEGEMANN, J. PFAFF, AND R. J. SAYKALLY, *Phys. Rev. Lett.* **50**, 727-731 (1983).
8. P. R. BUNKER, T. AMANO, AND V. ŠPIRKO, *J. Mol. Spectrosc.* **107**, 208-211 (1984).

NATHAN N. HAESE¹
DI-JIA LIU²
TAKESHI OKA

Department of Chemistry and
Department of Astronomy and Astrophysics
The University of Chicago
Chicago, Illinois 60637
Received February 22, 1988

¹ Present address: Dow Chemical Co., P.O. Box 9002, Walnut Creek, CA 94598.

² Present address: Department of Chemistry, University of California, Berkeley, CA 94720.