Mitsunori Araki, Hiroyuki Ozeki, and Shuji Saito

Experimental determination of the ground-state inversion splitting in D_3O^+ by microwave spectroscopy

Mitsunori Araki, Hiroyuki Ozeki, and Shuji Saito
The Graduate University for Advanced Studies and Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Inversion–rotation transitions of the fully deuterated hydronium ion, D_3O^+, were observed for the first time by microwave spectroscopy. The ion was generated in a hollow cathode cell by dc-glow discharge of a mixture of D_2O and D_2. Twenty six P- and Q-branch transitions were measured precisely for the lowest pair levels of inversion motion in the frequency region of 220–565 GHz. The ground-state inversion splitting and effective molecular constants for the upper and lower levels were determined by a least-squares fit of the measured line frequencies. The inversion splitting was determined to be 15.355 504 4(45) cm^{-1}, where the number in parentheses denotes three standard deviations of the fit. © *1998 American Institute of Physics.* [S0021-9606(98)02538-0]

The hydronium ion, H_3O^+, is one of the most fundamental species in aqueous acid–base chemistry, and also in gas-phase interstellar chemistry. The ion is isoelectronic to ammonia showing an ''umbrella inversion motion'' and has been extensively studied spectroscopically. The first high-resolution spectroscopy of the gaseous H_3O^+ ion was carried out by Begemann *et al.* in 1983[1,2] who reported the laser infrared study of the ν_3 band. Since then several experimental studies have been devoted to the ν_2 band, all of which focused on determining the tunneling splitting for the inversion motion.[3–6] However, a direct measurement of the tunneling doublet, which was essential to locate the lowest absolute energy levels of H_3O^+, was not successful until 1985.[5,7] Liu and Oka measured the crucial inversion separation in the $\nu_2 = 1$ state, $1^- - 1^+$, and derived the ground state splitting for the first time.[5,7,8] Soon after this study the separation was refined by direct observation with submillimeter-wave and far-infrared spectroscopy.[9–12] In the meantime, theoretical studies had been developed to predict the potential surface and the rotation–inversion–vibration energy levels of H_3O^+.[13–18]

In contrast to the normal species, spectroscopic studies of the fully deuterated species, D_3O^+, are extremely limited. So far two infrared studies were reported on the vibration-rotation transition of ν_2 (Ref. 19) and ν_3,[20] but the inversion splitting in the zeroth vibrational level was predicted only by using a nonrigid inverter model. The experimental determination of the splitting of D_3O^+ is as equally crucial as that of H_3O^+.[21] We report the first direct observation of the inversion splitting of the D_3O^+ ion by microwave spectroscopy.

The inversion–rotation spectra of D_3O^+ were measured using the same experimental apparatus as that described previously.[22] The ion was generated in a free space absorption cell by a hollow cathode discharge of a mixture of D_2O and D_2 gases. A Pyrex glass cell of 2 m length and 10 cm outer diameter was cooled by circulating liquid nitrogen through a copper tube soldered onto a copper sheet covering the glass cell. The length of the hollow cathode was 1.3 m.

At first, intensity of a H_3O^+ line was monitored and its optimum conditions were deduced. These same conditions were used for the initial observation of the D_3O^+ ion. Spectral lines of the D_3O^+ ion were initially searched on the basis of the calculated inversion spectrum obtained from an analysis with a nonrigid inverter Hamiltonian by Sears *et al.*[19] They predicted that the strong Q-branch transitions $J=K$ ($K=1,2,3,...$) lie around 460–470 GHz. We found a series of lines that appeared from 459.9 GHz and showed the same production behavior. Their signal intensities decreased to one-half or one-third when a magnetic field of several tens of Gauss was also applied to the cell,[23,24] as shown in Fig. 1. The same magnetic-field behavior was also observed for lines of H_3O^+. The spectral lines were readily assigned to Q-branch transitions with $J=K$. These assignments enabled us to predict another series of Q-branch and P-branch transitions with high accuracy. So far we observed 5 P-branch and 21 Q-branch transitions in the frequency region between 220 and 565 GHz. Optimum conditions for the production of D_3O^+ were partial pressures of 15 mTorr of D_2O and 2 mTorr of D_2 and a discharge current of 400 mA. The cell
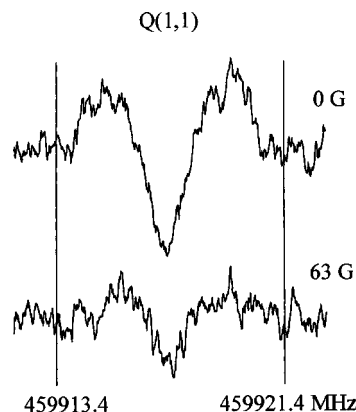

FIG. 1. The $Q(1,1)$ transition of D_3O^+ obtained with a integration time of 290 s (1600 scans). The upper trace was obtained without a magnetic field, whereas a field of 63 Gauss was applied in recording the lower trace.

5707

TABLE I. Observed transition frequencies of D_3O^+ (MHz).

$J^{p'}-J^{p}$ [a]		K	ν_{obs}^{b}	$\nu_{corr.}^{c}$	$\Delta\nu^{d}$
1^-	1^+	1	459 917.791(38)	459 917.710	−0.019
2^-	2^+	2	460 493.132(14)	460 493.051	−0.052
3^-	3^+	3	462 074.692(7)	462 074.611	0.060
4^-	4^+	4	464 669.162(15)	464 669.080	0.043
5^-	5^+	5	468 288.635(15)	468 288.552	0.041
6^-	6^+	6	472 949.967(13)	472 949.884	−0.049
7^-	7^+	7	478 675.348(13)	478 675.264	−0.040
8^-	8^+	8	485 491.826(10)	485 491.741	0.028
2^-	2^+	1	456 211.479(12)	456 211.399	−0.194[e]
3^-	3^+	2	454 940.389(14)	454 940.309	−0.011
4^-	4^+	3	454 664.410(17)	454 664.331	−0.414[e]
5^-	5^+	4	455 380.853(16)	455 380.774	0.012
6^-	6^+	5	457 089.243(19)	457 089.163	0.005
7^-	7^+	6	459 795.652(12)	459 795.571	−0.043
8^-	8^+	7	463 510.799(12)	463 510.718	0.010
10^-	10^+	9	474 033.831(15)	474 033.748	0.021
11^-	11^+	10	480 887.578(21)	480 887.494	−0.007
12^-	12^+	11	488 841.778(38)	488 841.692	−0.003
4^-	4^+	2	447 644.215(23)	447 644.137	0.881[e]
5^-	5^+	2	438 693.403(50)	438 693.326	0.002
6^-	6^+	2	428 204.134(69)	428 204.059	−0.728[e]
2^+	1^-	0	221 760.208(12)	221 760.169	0.057
2^+	1^-	1	220 397.505(23)	220 397.466	−0.057
3^+	2^-	0	565 066.727(29)	565 066.628	−0.023
3^+	2^-	1	563 748.641(36)	563 748.542	0.184[f]
3^+	2^-	2	559 770.314(29)	559 770.216	0.005

[a]The sign p expresses levels of the inversion splitting, where + and − signs indicate lower and upper levels and correspond to s and a in Ref. 20.
[b]Values in parentheses denote one standard deviation of the frequency measurement and apply to the last digits of the frequencies.
[c]Observed frequencies corrected by the ion-drift Doppler shift. The values were used in the least squares fit.
[d]$\Delta\nu = \nu_{corr.} - \nu_{calc.}$.
[e]Not included in the least squares fit.
[f]Weight is 0.1.

temperature was maintained between −15 and −35 °C.

The observed frequencies include ion-drift Doppler shifts as a relatively high voltage (a thousand volts) was applied to the discharge cell. The amount of the shift was estimated by measuring the difference between the observed frequencies of the two strong lines at 455 GHz ($Q(J,K)$ = (4,3) and (5,4)) with normal and opposite electrode configurations, where microwave radiation was propagated from the anode to the cathode in the normal configuration and vice versa in the opposite. The difference between measured frequencies with both configurations was 160 kHz, and was used to correct observed line frequencies around 455 GHz; all other observed line frequencies were similarly corrected using the same proportionality factor. The rotational state dependency of ionic mobilities was considered to be less than 10% of the Doppler shifts.[25,26] This gives only uncertainties of about 16 kHz to the errors of the ion drift corrected frequencies. These uncertainties are comparable to or less than the frequency measurement errors in the present study (Table I). The observed and ion-drift corrected frequencies are listed in Table I.

Molecular constants were determined by a least-squares fit of the corrected frequencies to an inversion–rotation energy formula, composed of typical symmetric-top rotation energies for the 0^+ and 0^- levels and the inversion splitting. No off-diagonal interactions were included in the analysis, which connected the basis functions of $\Delta K = \pm 3n$.[12,27,28] The determined molecular constants are listed in Table II. The standard deviation of the fit was 53 kHz. This relatively large value may be due to the relatively large line widths at 400–500 GHz, as shown in Fig. 1. The centrifugal distortion constant $D_{JK}(0^-)$ ($= -14.0168(100)$ MHz) obtained in the present study differs significantly from the previously reported values, $-22.60(198)$ (Ref. 19) and $-10.89(50)$ (Ref. 20) MHz, which were obtained by observations in the infrared region. We used a Hamiltonian with higher order terms, but inclusion of $H_{JK}(0^-)$ and $H_K(0^-)-H_K(0^+)$ did not give a significant change in the determination of $D_{JK}(0^-)$. Such a large deviation may arise from a limited number of P-branch component lines, and rotational and centrifugal distortion constants, B, D_J, D_{JK}, and H_{JK} for the upper (0^-) and lower (0^+) inversion levels, were not completely distinguishable in the least-squares fit. Further measurements of P- or R-branch transitions in the far infrared region will make it possible to obtain more accurate and reliable constants. Since any transitions with quantum number K being changed by 3 were not observed, no information on C constants and other K-dependent terms were deduced except for differences between the two states. On the contrary, we were able to determine the ground state inversion splitting accurately to be

TABLE II. Molecular constants of the $\nu=0^+$, 0^- states of D_3O^+ (MHz).

Molecular constant	Present study	IR[a]	IR[b]
$\nu(0^--0^+)$	460 346.441(134)[c]		
$(C-B)(0^-)-(C-B)(0^+)$	1 433.712(43)		
$D_K(0^-)-D_K(0^+)$	−2.071 95(121)	−2.42(68)	
$H_K(0^-)-H_K(0^+)$	0.000 067 35(91)		
$B(0^-)$	169 198.934(63)	169 192.4(72)	169 188.8(90)
$D_{JK}(0^-)$	−14.016 8(100)	−10.89(50)	−22.60(198)
$D_J(0^-)$	7.587 4(39)	7.57(22)	6.84(63)
$H_{JK}(0^-)$	−0.000 053 4(60)		
$B(0^+)$	170 130.270(66)	170 131.7(55)	170 131.6(64)
$D_{JK}(0^+)$	−16.833 6(108)	−16.935(198)	−16.89(24)
$D_J(0^+)$	8.539 8(43)	8.547(83)	8.535(99)

[a]Reference 20.
[b]Reference 19.
[c]Values in parentheses denote three times the standard deviations, and apply to the last digits of the constants.

460 346.441(134) MHz (15.355 504 4(45) cm^{-1}), where the errors in parentheses denote three times the standard deviation and apply to the last digits. This is completely due to the measurements of a number of Q-branch transitions with microwave spectroscopic precision. The experimental determination of the splitting in the zeroth vibrational level leads to refine the splitting in the vibrationally excited state. Using infrared laser spectroscopy, Petek *et al.* determined the $1^- - 0^+$ and the $1^+ - 0^-$ transitions of the ν_2 band to be 645.130 43(111) and 438.386 19(183) cm^{-1}, respectively.[20] We calculated the splitting width for the ν_2 excited state to be 191.3887(30) cm^{-1}, where the error is mostly due to the experimental uncertainty of the infrared study. The present result agrees well with the theoretically predicted value using the nonrigid invertor model, which varied from 15.2 to 15.7 cm^{-1}.[19,21] The determined value of $(C-B)(0^-)$ $-(C-B)(0^+)$ was also found to lie within the prediction.[19,21] Further spectral measurements and analysis are now in progress for refining the molecular constants of the D$_3$O$^+$ ion. The ground-state inversion splitting of the present study is essential to a deep understanding of the inversion potential of H$_3$O$^+$.

[1] M. H. Begemann, C. S. Gudeman, J. Pfaff, and R. J. Saykally, Phys. Rev. Lett. **51**, 554 (1983).

[2] M. H. Begemann and R. J. Saykally, J. Chem. Phys. **82**, 3570 (1985).

[3] N. N. Haese and T. Oka, J. Chem. Phys. **80**, 572 (1984).

[4] B. Lemoine and J. L. Destombes, Chem. Phys. Lett. **111**, 284 (1984).

[5] D.-J. Liu, N. N. Haese, and T. Oka, J. Chem. Phys. **82**, 5368 (1985).

[6] P. B. Davies, P. A. Hamilton, and S. A. Johnson, J. Opt. Soc. Am. B **2**, 794 (1985).

[7] D.-J. Liu and T. Oka, Phys. Rev. Lett. **54**, 1787 (1985).

[8] D.-J. Liu, T. Oka, and T. Sears, J. Chem. Phys. **84**, 1312 (1986).

[9] G. M. Plummer, E. Herbst, and F. C. Delucia, J. Chem. Phys. **83**, 1428 (1985).

[10] M. Bogey, C. Demuynck, M. Demis, and J. L. Destombes, Astron. Astrophys. **148**, L11 (1985).

[11] P. Verhoeve, J. J. terMeulen, W. L. Meerts, and A. Dymanus, Chem. Phys. Lett. **143**, 501 (1988).

[12] P. Verhoeve, M. Versluis, J. J. terMeulen, W. L. Meerts, and A. Dymanus, Chem. Phys. Lett. **161**, 195 (1989).

[13] V. Špirko and P. R. Bunker, J. Mol. Spectrosc. **95**, 226 (1982).

[14] P. R. Bunker, W. P. Kraemer, and V. Špirko, J. Mol. Spectrosc. **101**, 180 (1983).

[15] P. Botschwina, P. Rosmus, and E.-A. Reinsch, Chem. Phys. Lett. **102**, 299 (1983).

[16] N. Shida, K. Tanaka, and K. Ohno, Chem. Phys. Lett. **104**, 575 (1984).

[17] P. R. Bunker, T. Amano, and V. Špirko, J. Mol. Spectrosc. **107**, 208 (1984).

[18] V. Danielis and V. Špirko, J. Mol. Spectrosc. **117**, 175 (1986).

[19] T. J. Sears, P. R. Bunker, P. B. Davies, S. A. Johnson, and V. Spirko, J. Chem. Phys. **83**, 2676 (1985).

[20] H. Petek, D. J. Nesbitt, J. C. Owrutsky, C. S. Gudeman, X. Yang, D. O. Harris, C. B. Moore, and R. J. Saykally, J. Chem. Phys. **92**, 3257 (1990).

[21] V. Špirko and W. P. Kraemer, J. Mol. Spectrosc. **134**, 72 (1989).

[22] S. Saito and M. Goto, Astrophys. J. **410**, L53 (1993).

[23] S. Saito, K. Kawaguchi, and E. Hirota, J. Chem. Phys. **82**, 45 (1985).

[24] K. Kawaguchi, C. Yamada, S. Saito, and E. Hirota, J. Chem. Phys. **82**, 1750 (1985).

[25] N. N. Haese, F.-S. Pan, and T. Oka, Phys. Rev. Lett. **50**, 1575 (1983).

[26] C. S. Gudeman and R. J. Saykally, Annu. Rev. Phys. Chem. **35**, 387 (1984).

[27] S. P. Belov, L. I. Gershstein, A. F. Krupnov, A. V. Maslovsky, S. Urban, V. Špirko, and D. Papousek, J. Mol. Spectrosc. **84**, 288 (1980).

[28] D. Uy, E. T. White, and T. Oka, J. Mol. Spectrosc. **183**, 240 (1997).