# Experimental Determination of the Ground-State Inversion Splitting in $H_3O^+$

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The ground-state inversion splitting of the $H_3O^+$ molecular ion has been determined to be $55.3462 \pm 0.0055$ cm$^{-1}$ from the high-resolution laser infrared spectroscopy of the $\nu_2$ band. This has enabled us to predict accurately the ground-state inversion spectrum in the far-infrared region and the inversion-rotation spectrum in the millimeter-wave region which may be used to detect this fundamental molecular ion in interstellar space.

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The occurrence of the $NH_3$ inversion spectrum in the microwave region is a great accident of nature which was crucial in the development of microwave spectroscopy,[1] the invention of the maser,[1] and the discovery of polyatomic molecules in interstellar space.[2] The measurement of the inversion frequency in the ground vibronic state has so far been limited to $NH_3$ and its related compounds such as its isotopic species and amino and imino compounds. The inversion frequency of $PH_3$, the next compound of the same group, is lower by at least $10^8$ and even the highest-resolution molecular-beam spectrometer cannot resolve the splitting[3] ($\Delta\nu < 1$ kHz).

In this paper we report our experimental determination of the ground-state inversion splitting in the $H_3O^+$ molecular ion. This ion, which is one of the most fundamental and important molecular ions, is isoelectronic to $NH_3$ and hence also has a pyramidal structure and a double-minimum potential (see Fig. 1). The early calculations by Diercksen, Kraemer, and Roos[5] and by Novick, Stevens, and Klemperer[6] predicted the ground-state inversion splitting to be in the far-infrared region at ~83 cm$^{-1}$. More recent theoretical calculations[7-9] gave lower predicted values between 72[7] and 46 cm$^{-1}$.[8] The accurate experimental determination of this value is of prime importance because it allows astronomers to search for this species in space by means of the far-infrared and microwave spectrum. $H_3O^+$ is predicted to exist in abundance in molecular clouds.[10, 11]

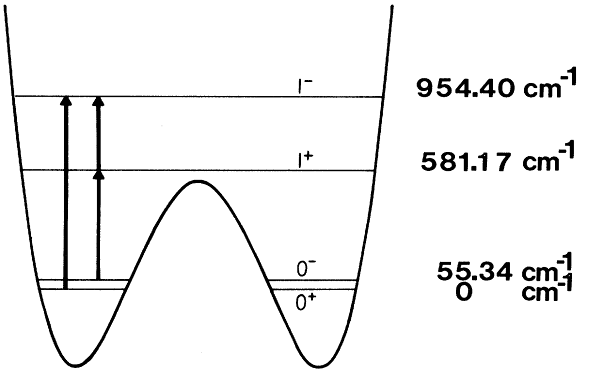

FIG. 1. The double minimum potential and the vibration-inversion energy levels of the $\nu_2$ bending mode of $H_3O^+$. The three infrared bands $1^- \leftarrow 0^+$, $1^+ \leftarrow 0^-$, and $1^- \leftarrow 1^+$ shown by the bold arrows appear at 10.5, 19, and 27 $\mu$m, respectively. The ground-state inversion splitting has been determined from the measurement of the $1^- \leftarrow 1^+$ band, reported in this paper, and our previous measurements of the other two bands (Ref. 4).

The experiment is now possible because of the rapid development of laser infrared ion spectroscopy which occurred in the last several years. Following the success of observing the high-resolution infrared ion spectrum of $HD^+$ by Wing *et al.*, using the ingenious ion-beam laser resonance technique,[12] the introduction of tunable laser infrared sources combined with discharges[13] and the development of the velocity-modulation technique by Gudeman *et al.*[14] have made it possible to apply the laser infrared spectroscopy to many molecular ions. The method was used to discover the infrared spectrum of $H_3O^+$ in the 3-$\mu$m region by Begemann *et al.*[15]

We initiated diode laser spectroscopy of $H_3O^+$ in the lower-frequency infrared region where absorption bands related to the $\nu_2$ bending-inversion vibration are expected. First the 10-$\mu$m $1^- \leftarrow 0^+$ band was observed at 954.4003 cm$^{-1}$.[16] On the basis of this result Bunker, Amano, and Spirko[17] revised their earlier calculation[7] and predicted band origins and rotational constants for other bands. The second band, $1^+ \leftarrow 0^-$, was observed at 525.8237 cm$^{-1}$.[4] These two bands have also been studied by Lemoine and Destombes[18] and by Davies, Hamilton, and Johnson.[19] We now have determined the crucial $1^-$-$1^+$ separation to be $373.2305 \pm 0.0047$ cm$^{-1}$, which fixes the ground-state splitting to be $55.3462 \pm 0.0055$ cm$^{-1}$. This enables us to predict the ground-state inversion and the inversion-rotation spectrum accurately. The experimentally determined inversion splitting is very close to the most recent theoretical prediction by Bunker[20] of 54.695 cm$^{-1}$.

The apparatus used for the spectroscopy of the 26-

$\mu$m $1^- \leftarrow 1^+$ band was similar to that reported earlier. Four Mesa-stripe geometry diodes from Laser Analytics were used as radiation sources. The infrared radiation, passed through a water-cooled discharge tube (12 mm i.d., 80 cm long) and a monochromator, was detected by a Ge:Cu detector. The $H_3O^+$ ion was generated in the ac discharge cell from an $O_2/H_2$ mixture with the ratio of $\sim 1{:}8$.[4] The $H_3O^+$ absorption signal which was modulated because of the velocity modulation of ions in the alternating field of the discharge was processed by a phase-sensitive detector.[14] A group of lines close to the band origin, which played the crucial role for the identification of the $1^- \leftarrow 1^+$ band, is shown in Fig. 2. Since this transition is essentially an inversion transition in the $\nu_2 = 1$ excited state, the transition dipole moment is very large (predicted to be 1.1 D by Botschwina, Rosmus, and Reinsch.[8]). Therefore, although the population of ions in the $1^+$ level is less than that in the $0^{\pm}$ levels, fairly strong signals were recorded. Frequencies of the observed lines were measured with use of the known $CS_2$ spectrum reported by Jolma and Kauppinen.[21] The accuracy of our frequency measurements is estimated to be 0.005 cm$^{-1}$.

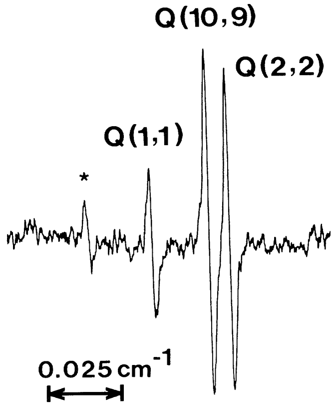

FIG. 2. The group of lines close to the origin of the $1^- \leftarrow 1^+$ band. The derivative shape is due to velocity modulation (Ref. 14). The line with the asterisk is most likely the ground-state inversion-rotation transition $R(15, 9)$. Time constant of detection is 3 sec.

Observed frequencies, their assignments, and the deviations are shown in Table I. Four lines which were earlier measured[4] in the 20-$\mu$m region but were left unassigned to the $1^+ \leftarrow 0^-$ band were found to be $R$-branch lines of the $1^- \leftarrow 1^+$ band. Altogether sixteen lines were measured and thirteen of them were assigned to the $1^- \leftarrow 1^+$ band. The frequencies of the remaining three are 386.4885, 379.9907, and 372.8882 cm$^{-1}$. These frequencies agree well with the calculated positions for the $R(15,12)$, $R(16,3)$, and $R(15,9)$ transitions of the $0^- \leftarrow 0^+$ band though definite assignment needs more confirming lines. The observed frequencies were fitted by the symmetric rotor energy levels with use of rotational constants up to the quartic centrifugal distortion. The determined molecular constants are shown in Table II. The quality of the least-squares fitting is lower than that for our previous work on the $1^- \leftarrow 0^+$ and the $1^+ \leftarrow 0^-$ bands[4] for rotational constants because of fewer measured lines and the missing $P$-branch transitions. However, the good agreement of the constants with those previously determined[4] makes us confident of the correctness of the present assignment and the newly determined value of the inversion splitting. We plan to improve the accuracy by increasing the number of measured lines, but a dramatic improvement of the situation is not likely for some time because these fre-

TABLE I. Observed spectral lines of the $1^- \leftarrow 1^+$ band (in inverse centimeters).

| Transitions | Observed frequencies | Obs. − Calc. ($\times 10^3$) |
|---|---|---|
| $R(9,3)$ | 548.289 | 0 |
| $R(9,2)$ | 545.028 | 0 |
| $R(7,7)$ | 548.718 | 0 |
| $R(5,2)$ | 489.336 | 0 |
| $Q(9,9)$ | 382.496 | −3 |
| $Q(8,8)$ | 380.174 | 2 |
| $Q(13,12)$ | 378.910 | 4 |
| $Q(7,7)$ | 378.154 | 1 |
| $Q(12,11)$ | 376.621 | −6 |
| $Q(3,3)$ | 373.324 | 7 |
| $Q(2,2)$ | 372.941 | −5 |
| $Q(10,9)$ | 372.933 | 1 |
| $Q(1,1)$ | 372.913 | −3 |

TABLE II. Molecular constants of the observed $1^-$-$1^+$ band and derived $0^-$-$0^+$ band (in inverse centimeters).

| Molecular constants | $1^- \leftarrow 1^+$ | $0^- \leftarrow 0^+$ |
|---|---|---|
| Inversion splitting | 373.2304(47)[a] | 55.3462(55) |
| $(c' - B') - (c'' - B'')$ | 0.6583(35) | 0.2801(35) |
| $(D_K' - D_K'') \times 10^4$ | −0.13(25) | −6.04(27) |
| $B'$ | 10.6973(56) | 11.0558[b] |
| $B''$ | 11.1836(84) | 11.2537[b] |
| $D_J' \times 10^4$ | 4.68(34) | 10.08[b] |
| $D_J'' \times 10^4$ | 5.78(56) | 13.02[b] |
| $D_{JK}' \times 10^4$ | −4.7(12) | −17.02[b] |
| $D_{JK}'' \times 10^4$ | −6.4(13) | −27.51[b] |

[a] Values in the parentheses are 1 standard deviation of the least-squares fitting.

[b] Values from our previous work (Ref. 4).

TABLE III. Predicted inversion and inversion-rotation spectrum of $H_3O^+$ related to the metastable rotational levels (in inverse centimeters). Numbers in parenthesis are the uncertainties of the prediction (1 standard deviation).

| Transitions | Frequencies |
|---|---|
| $R(3,3)$ | 143.781(38) |
| $R(3,0)$ | 141.202(13) |
| $R(2,2)$ | 121.541(17) |
| $R(1,1)$ | 99.428(7) |
| $Q(3,3)$ | 55.470(35) |
| $Q(2,2)$ | 55.274(16) |
| $Q(1,1)$ | 55.230(7) |
| $P(1,0)$ | 32.844(6) |
| $P(2,1)$ | 10.246(8) |
| $P(3,2)$ | (−)12.173[a](17) |
| $P(3,1)$ | (−)12.954[a](10) |
| $P(3,0)$ | (−)13.212[a](10) |

[a] For those transitions the $0^+$ level is above the $0^-$ level.

quencies represent almost the lower limit at present of commercially available diode lasers. More measurements of rotation-inversion transitions associated with the ground vibrational state mentioned earlier may improve the situation considerably.

Detection of the far-infrared inversion transitions and the millimeter-wave inversion-rotation transitions of $H_3O^+$ in space and in the laboratory is an exciting possibility. For such a purpose we list in Table III the predicted frequencies based on the constants listed in Table II. Only transitions related to metastable rotation-inversion levels[22] and millimeter-wave transitions are listed for conciseness of the table. Others can be calculated from the constants given in Table II.

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