

SUB-MILLIMETER LASER SIDEBAND SPECTROSCOPY OF  $\text{H}_3\text{O}^+$ 

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We report the observation of three rotation-inversion transitions around  $35\text{ cm}^{-1}$  in the  $\nu=0^- \leftarrow 0^+$  band of  $\text{H}_3\text{O}^+$ . Spectra were recorded using a sub-millimeter laser sideband spectrometer. An improved set of molecular constants for the  $\nu=0^-$  and  $0^+$  states and more accurate predictions for the Q-branch transitions of this band are obtained.

## 1. Introduction

The hydronium ion  $\text{H}_3\text{O}^+$  has been the subject of much spectroscopic and theoretical work in the last few years. The ion is expected to be rather abundant in interstellar clouds [1,2] and to play an important role in the interstellar OH and  $\text{H}_2\text{O}$  chemistry, but it has not been detected yet. Accurate values for the frequencies between the lowest rotational states are crucial for its discovery in the interstellar space.  $\text{H}_3\text{O}^+$  has a pyramidal structure similar to the isoelectronic  $\text{NH}_3$  molecule and accordingly it shows an inversion spectrum associated with the tunneling motion of the oxygen atom through the plane of the hydrogen atoms. Ab initio calculations [3-7] showed that the inversion splitting between the lowest vibrational levels ( $0^+$  and  $0^-$ ) should be about  $50\text{ cm}^{-1}$ . Thus, transitions of the  $0^- \leftarrow 0^+$  band occur in the sub-millimeter region. This was confirmed by the observations of several bands of the  $\nu_2$  vibration in the infrared [8-13] and four transitions in the sub-millimeter region [14,15]. Furthermore, bands of the  $\nu_3$  [16-19] and  $\nu_4$  [20] vibrations have been observed. A least-squares fit of all previous data on the  $\nu_2$  vibration has been performed by Liu et al. [13].

In this paper we present the observation of three more transitions of the  $0^- \leftarrow 0^+$  band in the far infrared. The transitions are indicated in an energy level scheme in fig. 1 together with the sub-millimeter transitions observed by Plummer et al. [14] and Bogey et al. [15]. One of these transitions is of particular interstellar interest since it involves the low-

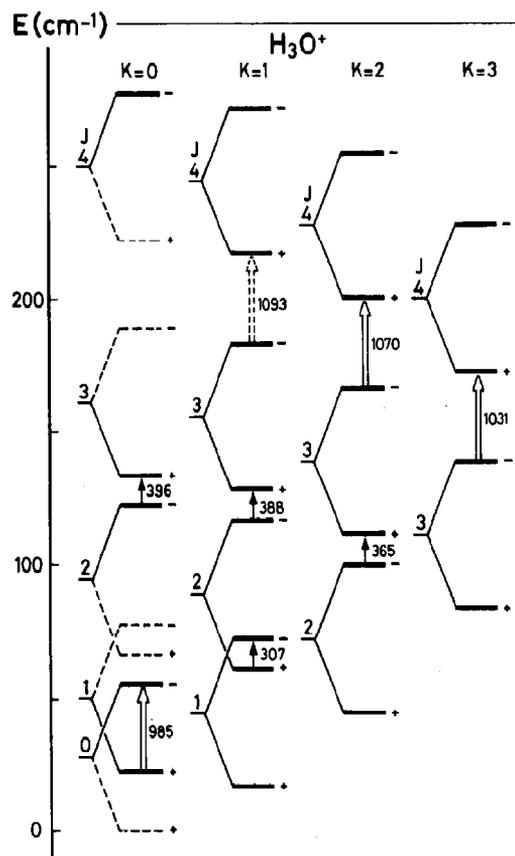


Fig. 1. Energy level scheme ([15], modified) showing the lowest rotational levels of the  $\nu=0^-$  and  $0^+$  states. The narrow arrows are the transitions from refs. [14,15]. The wide arrows are the transitions from this work. The transitions with the dotted arrow could not be observed. The numbers indicate the transition frequencies in GHz.

lying  $(J,K) = (1,0)^+$  state. An improved set of molecular parameters for the  $0^-$  and  $0^+$  levels as well as more accurate predictions for the Q-branch transitions are obtained.

## 2. Experimental details

The transitions of  $\text{H}_3\text{O}^+$  were observed with the far-infrared laser sideband spectrometer described in detail in ref. [21]. The ions were produced in a water-cooled hollow cathode discharge of  $\text{H}_2$  (10 Pa) and  $\text{H}_2\text{O}$  (2 Pa). As observed by other groups [13,15], the signals could also be observed using  $\text{O}_2$  instead of  $\text{H}_2\text{O}$  with a somewhat smaller intensity. Cooling the discharge did not improve the signals. The discharge current was 0.5 A. In order to allow phase-sensitive detection, a modulation of the discharge current at about 330 Hz was applied, thus modulating the production of short-lived ionic species and suppressing signals of long-lived neutral species. Signals were recorded with a few microwatt of sideband power.

## 3. Results and analysis

Three inversion-rotation transitions around  $35\text{ cm}^{-1}$  in the P branch of the  $0^- \leftarrow 0^+$  band of  $\text{H}_3\text{O}^+$  have been observed. Their frequencies with experimental uncertainties are listed in table 1 together with the frequencies predicted by Liu et al. [13]. All three transitions were found within 30 MHz from the predicted frequencies. Once we had detected two transitions, the third one could be calculated with an uncertainty of less than 2 MHz and was detected within 1 MHz from this position. A fourth transition

Table 1  
Observed transitions in the  $0^- \leftarrow 0^+$  band of  $\text{H}_3\text{O}^+$  (in  $\text{cm}^{-1}$ )

$(J',K') \leftarrow (J'',K'')$	This work	Predicted frequencies [13]
$(0,0)^- \leftarrow (1,0)^+$	32.84646(3)	32.8454
$(4,3)^+ \leftarrow (3,3)^-$	34.40025(3)	34.3998
$(4,2)^+ \leftarrow (3,2)^-$	35.68557(4)	35.6860

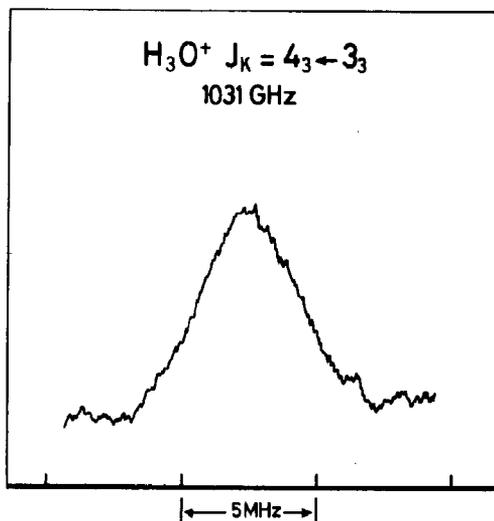


Fig. 2. Recording of the  $(J,K) = (4,3)^+ \leftarrow (3,3)^-$  transitions with a 3 s RC time.

near  $35\text{ cm}^{-1}$ ,  $(J,K) = (4,1)^+ \leftarrow (3,1)^-$ , that lies within the spectral range of the spectrometer, could not be observed because of absorption of sideband power by atmospheric water vapor. Fig. 2 shows one of the measured transitions. The experimental linewidth is  $\approx 4.5\text{ MHz}$ .

The measured frequencies were fitted to the following expression for the transition frequencies for parallel bands of symmetric top molecules [13]:

$$\begin{aligned} \nu = \nu_0 + & [(C'' - B'') - (C' - B')]K^2 \\ & - (D_K'' - D_K')K^4 + B''J''(J'' + 1) \\ & - [D_{JK}''K^2 + D_J''J''(J'' + 1)]J''(J'' + 1) \\ & - B'J'(J' + 1) \\ & + [D_{JK}'K^2 + D_J'J'(J' + 1)]J'(J' + 1), \end{aligned} \quad (1)$$

where  $\nu_0$  is the band origin,  $B$  and  $C$  are rotational constants,  $D_K$ ,  $D_{JK}$  and  $D_J$  are centrifugal distortion constants and  $J$  and  $K$  are rotational quantum numbers. In the least-squares fit, also the reported submillimeter data [14,15] and the infrared data collected in ref. [13] were included. All frequencies were weighted according to their experimental uncertainties. The infrared data were assumed to have an uncertainty of  $0.005\text{ cm}^{-1}$ . The results are listed in table 2 and compared with the constants obtained by Liu et al. [13] from their fit of the same data with the exception of the presently observed frequencies of

Table 2

Molecular constants of the  $\nu=0^+, 0^-, 1^+$  and  $1^-$  states of the  $\nu_2$  vibration of  $\text{H}_3\text{O}^+$  (in  $\text{cm}^{-1}$ , unless indicated otherwise). Numbers in parentheses represent one standard deviation

	This work + refs. [8-15]	Ref. [13]	Ref. [19]
$\nu(1^- \leftarrow 0^+)$	954.4015(10)	954.4001(12)	
$\nu(1^+ \leftarrow 0^-)$	525.8268(10)	525.8266(11)	
$\nu(1^- \leftarrow 1^+)$	373.2246(11)	373.2254(13)	
$\nu(0^- \leftarrow 0^+)$	55.35006(6)	55.3481(21)	
$(C-B)(1^-) - (C-B)(0^+)$	0.68718(8)	0.68649(12)	
$(C-B)(1^+) - (C-B)(0^-)$	-0.25173(8)	-0.25180(11)	
$(C-B)(1^-) - (C-B)(1^+)$	0.65698(12)	0.65686(10)	
$(C-B)(0^-) - (C-B)(0^+)$	0.281924(14)	0.28143(19)	
$B(1^-)$	10.69730(8)	10.69741(12)	
$B(1^+)$	11.18248(8)	11.18247(14)	
$B(0^-)$	11.05496(4)	11.05486(14)	11.0550(3)
$B(0^+)$	11.25446(2)	11.25397(15)	11.2547(2)
$D_J(1^-)^{a1}$	5.116(15)	5.16(2)	
$D_J(1^+)$	6.32(2)	6.37(3)	
$D_J(0^-)$	10.022(12)	10.04(2)	10.12(8)
$D_J(0^+)$	13.307(8)	13.08(3)	13.329(37)
$D_{JK}(1^-)$	-5.80(4)	-5.87(5)	
$D_{JK}(1^+)$	-7.84(5)	-7.97(6)	
$D_{JK}(0^-)$	-18.40(3)	-18.48(5)	-18.71(23)
$D_{JK}(0^+)$	-27.45(3)	-26.91(8)	-27.319(81)
$D_K(1^-) - D_K(0^+)$	-14.19(2)	-13.85(3)	
$D_K(1^+) - D_K(0^-)$	-7.72(3)	-7.69(3)	
$D_K(1^-) - D_K(1^+)$	-0.36(3)	-0.42(2)	
$D_K(0^-) - D_K(0^+)$	-6.108(8)	-5.74(7)	-5.71(17)

<sup>a1</sup> All centrifugal distortion parameters are in  $10^{-4} \text{cm}^{-1}$ .

table 1. It should be noted that Liu et al. gave the sub-millimeter data of refs. [14,15] only a 100 times greater weight than the infrared data, which does not fully exploit the experimental accuracy of these data. The fourth column in table 2 shows parameters obtained from a fit of all available earlier data of the  $\nu_2$  and  $\nu_3$  vibration bands by Stahn et al. [19]. It is seen that not all parameters are in agreement within the claimed accuracies.

Our fit also indicates, that, in addition to the deviating frequencies already mentioned by Liu et al. in their table 1 [13], the frequency of the R(7,0) transitions of the  $1^- \leftarrow 0^+$  band [9] is not in agreement with the value calculated in the fit. The difference between observed and calculated frequency is  $-0.064 \text{cm}^{-1}$ . This line was not included in the final fit. The frequencies of the Q-branch transitions of the  $0^- \leftarrow 0^+$  band can now be calculated within an uncertainty of 25 MHz up to  $J=5$ . Their values are listed in table 3.

Table 3

Calculated frequencies (in  $\text{cm}^{-1}$ ) for the Q-branch transitions up to  $J=5$  of the  $0^- \leftarrow 0^+$  band. Numbers in parentheses represent one standard deviation

(J,K)	Frequency
(1,1)	55.2331(2)
(2,1)	54.4420(3)
(2,2)	55.2806(3)
(3,1)	53.2750(4)
(3,2)	54.0973(4)
(3,3)	55.4924(4)
(4,1)	51.7558(5)
(4,2)	52.5564(5)
(4,3)	53.9153(5)
(4,4)	55.8691(5)
(5,1)	49.9159(9)
(5,2)	50.6894(8)
(5,3)	52.0031(6)
(5,4)	53.8936(6)
(5,5)	56.4121(7)

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