Astron. Astrophys. 148, L11–L13 (1985)

ASTRONOMY AND ASTROPHYSICS

Letter to the Editor

Laboratory measurement of the submillimeter wave spectrum of H_3O^+

M. Bogey, C. Demuynck, M. Denis, and J. L. Destombes

Université de Lille 1, Laboratoire de Spectroscopie Hertzienne, associé au C.N.R.S., F-59655 Villeneuve d'Ascq Cedex, France

Received May 7, accepted May 23, 1985

Summary : Three rotation-inversion lines of the H_3O^+ ion have been observed in the 360-396 GHz frequency range by using a magnetically confined glow discharge. The measured frequencies are in very good agreement with recent predictions derived from the infrared spectrum. They provide the basic data necessary for astrophycical search by submillimeter radioastronomy.

Key words : Millimeter lines, Spectroscopy, Molecular data.

In an effort to understand the chemical formation of complex interstellar molecules, sophisticated chemical networks have been developped during the last few years (GRAEDEL et al. 1984), with the main goal of determining whether or not gas phase chemistry can account for the number of chemical species observed in the interstellar medium. Among the reactive intermediate molecules involved in the chemical evolution of the interstellar clouds, some species play a key role although they have not been observationnally detected. This was the case of H_3^+ which has been detected only recently through its deuterated form H_2D^+ (PHILLIPS et al. 1985).

The H_3O^+ hydroxonium ion is another example of such a situation. This ion is formed in the first stages of the interstellar chemistry and it is thought to be the key ion of OH and H_2O chemistry (DALGARNO and BLACK 1976, WATSON 1978, SMITH and ADAMS 1981, GRAEDEL et al. 1982). In a pseudo time-dependent chemical modelling of dense clouds, LEUNG et al. (1984) have predicted a rather high abundance of this ion. In their low metal abundance model which seems to lead to a better agreement with observed molecular abundance, they have calculated a H_3O^+ fractional abundance ranging from 10^{-8} to 10^{-11} when the H_2 density increases from 10^3 cm^{-3} to 10^6 cm^{-3} respectively.

H_3O^+ is then a highly potential interstellar molecular ion, the detection of which could improve our knowledge of the interstellar chemistry to a great extent.

Although H_3O^+ has been the subject of extensive theoretical and experimental study, it is only in 1977 that it has been spectroscopically characterized in the gas phase (SCHWARTZ 1977). The high resolution spectroscopy of this ion is still more recent : the ν_3 IR band was first observed by BEGEMAN et al. (1983) by using velocity modulation technique. The $1^- - 0^+$ band of the ν_2 bending mode, first detected by HAESE and OKA (1984) has been investigated by LEMOINE and DESTOMBES (1984), and DAVIES et al. (1984) who also extended the analysis to the $1^+ - 0^-$ band (DAVIES et al. 1985). Very recently, LIU et al. (1985) and LIU and OKA (1985) reported the analysis of the $1^+ - 0^-$ and $1^- - 1^+$ bands, which allowed them to predict with a good accuracy the inversion splitting and the frequencies of the $0^- - 0^+$ millimeter lines which are of prime astrophysical interest, since the energy levels involved lie at about 90 cm^{-1} = 130 K (BUNKER 1985).

In this letter, we report the detection of the K = 0, 1, 2 components of the J = $2^- \rightarrow 3^+$ transitions occuring in the 300-400 GHz frequency range. A scheme of the involved energy levels is given on figure 1.

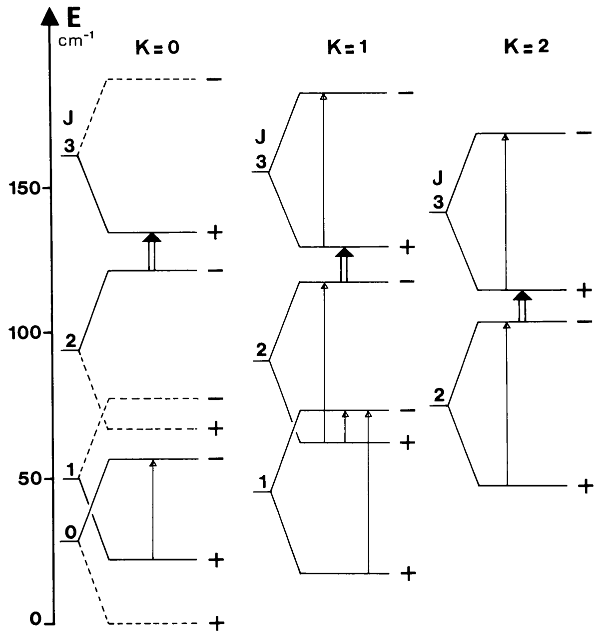

Figure 1 :
Energy level diagram showing allowed submillimeter transitions (single arrow) and observed transitions (double arrow). Level with 0 statistical weight are represented by dashed lines.

The submillimeter source used in this study is a phase-locked CSF carcinotron (TH4218D) operating in the 340-406 GHz frequency range. Detection is achieved by an InSb bolometer cooled at LHe temperature.

Phase lock of the carcinotron is achieved in a two step procedure involving a phase-locked millimeter wave klystron used as an intermediate frequency standard. The frequency of this klystron is harmonically mixed with the frequency of the carcinotron by using a Custom Microwave harmonic generator equiped with a Schottky diode. The + 520 MHz beat is used to phase

Send offprint requests to: J. L. Destombes

lock the carcinotron through an home made phase-lock stabilizer which will be described elsewhere. Frequency modulation (f = 12.5 kHz) is applied to the carcinotron by modulating the 520 MHZ reference frequency generated by an ADRET 6315 synthesizer. The signals are processed by a phase sensitive detection tuned at 2f = 25 kHz, which provides a second derivative line shape.

Wide frequency scans are achieved by programming step bu step the 5 MHz referenced synthesizer (ADRET 6100 B) which is used as a frequency standard for the phase-locked millimeterwave klystron.

To improve the S/N ratio, the phase sensitive detection can be followed by multichannel averaging. In that case, a dedicated microprocessor system is used to drive the repetitive frequency scan, to sample, digitize and store the spectroscopic repetitive waveform and to execute on the stored data some automatic data processings such as smoothing, base line suppression and frequency calculation (BOGEY et al. 1985).

The ions are created in a magnetically confined glow discharge (DE LUCIA et al. 1983), as previously used to observe H_2D^+ (BOGEY et al. 1984a) and HCO_2^+ (BOGEY et al. 1984b). The spectrum is best observed by discharging a mixture of H_2O ($p = 10^{-4}$ torr), H_2 ($p = 4.10^{-4}$ torr) and Ar ($p = 15.10^{-3}$ torr) at room temperature. The best discharge conditions are : I = 4mA, HV = 2000 v and the optimum magnetic field is B = 150 G.

In the first step of the search, a frequency range of ± 1.5 GHz was scanned around the $J = 2^- \to 3^+$ (K = 0 and 1) frequency predictions given by LIU and OKA (1985). Only two lines were observed, each of them well within the uncertainties predicted by these authors. In order to ascertain that these lines were due to H_3O^+, a number of tests have been done :

. opening the HV circuit leads to an immediate disappearance of the lines with no measurable time constant ;

. the lines exhibit a very characteristic behaviour versus magnetic field intensity, as emphasized on figure 2 : the peak absorption of the line is roughly proportional to the intensity of the field if B $\lesssim$ 150 G. Increasing further the field leads to a decrease of the line, a feature already observed on the H_2D^+ and HN_2^+ ions. By applying to the cell a transverse localized magnetic field (DE LUCIA et al. 1983) it is also easy to show that the line intensity is proportional to the length of the negative glow. All these behaviours are characteristic of an ionic species ;

. both H_2 and H_2O in convenient proportions are necessary. As observed by LIU and OKA (1985), mixtures of H_2 and O_2 give similar results ;

. cooling of the cell at liquid nitrogen temperature leads to the disappearance of the lines, as was observed on the IR H_3O^+ lines in a similar experiment (LEMOINE and DESTOMBES 1984) ;

. as will be seen below, it is possible to derive an accurate prediction of the $J = 2^- \to 3^+$ (K = 2) transition from the measured K = 0 and 1 ones, by using only one constant taken from the IR, namely $D_K^- - D_K^+$. The K = 2 line has been observed at less than 2 MHz from the predicted frequency, which leads to the definite confirmation that the observed ion is H_3O^+.

The three measured frequencies are presented in Table I.

From the standard expression of the energy levels of a symmetric top (GORDY and COOK 1984) written for the K = 0 component of the $J \to J' = 2^- \to 3^+$ transition :

$$\nu_{JJ'}(K) = \nu_{23}(0) = \nu(2^-, 0\to 3^+, 0)$$
$$= 12B^+ - 144D_J^+ - 6B^- + 36D_J^- - \nu_i$$

It is possible to derive a value of the inversion splitting ν_i by using the measured $\nu_{23}(0)$ frequency (table I) and the molecular constants derived from the IR spectrum by LIU and OKA (1985) and by DAVIES et al. (1985).

$(J,K)^- \to (J,K)^+$	measured frequency	predicted frequency (LIU and OKA, 1985)
2,0 → 3,0	396272.412 (60)	396086(300) a)
2,1 → 3,1	388458.641 (80)	388351(300) a)
2,2 → 3,2	364797.427(100)	364937(500) a)

TABLE I : Measured frequencies of H_3O^+

a) Numbers in the parenthesis are the uncertainties of the prediction (one standard deviation) from LIU and OKA (1985)

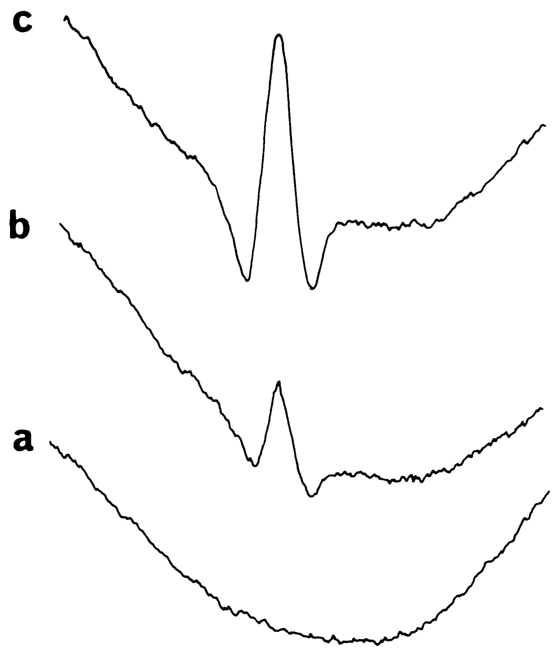

Figure 2 :
Evolution of the $\nu_{23}(0)$ line versus magnetic field :
a) B = 0 G ; b) = 75 G ; c) = 150 G.
The discharge current has been kept constant at I = 4 mA. Lock-in time constant = 100 msec.
Total pressure = 15 mtorr.

The two results are given in Table II, where they are compared to previous values and to results of ab initio calculations (SPIRKO and BUNKER 1982, BUNKER et al. 1983, BOTSCHWINA et al. 1983).

It is also easy to show that :

$$\nu_{23}(1) = \nu_{23}(0) + [(C^+-B^+)-(C^--B^-)-12D^+_{JK}-6D^-_{JK}+D^-_K-D^+_K]$$
$$= \nu_{23}(0) + \alpha$$

which leads to the value α(smm) = -7813.771(100) MHz = 0.2606393 cm^{-1}, in good agreement with the infrared value α(IR) = -0.257904 cm^{-1} (LIU and OKA 1985).

In the same way the frequency of the last line can be written as

$$\nu_{23}(2) = \nu_{23}(0) + 4\alpha + 12\ (D_K^- - D_K^+)$$
$$= 4\nu_{23}(1) - 3\nu_{23}(0) + 12\ (D_K^- - D_K^+)$$

from which an accurate value $D_K^- - D_K^+$ can be derived,

$D_K^- - D_K^+ = -18.325(40)$ MHz $= -6.113(13).10^{-4}$, a value in excellent agreement with the LIU and OKA value : $(D_K^- - D_K^+)_{IR} = -6.04(27).10^{-4}$ cm-1.

All these numerical results give a further confirmation that the ion we have observed is indeed H_3O^+. As only four transitions have frequencies below 1000 GHz, the determination of an accurate set of molecular parameters will need a global fit of infrared and submillimeter data.

ν_i	Reference
55.3402	This work + IR results from LIU and OKA (1985)
55.3616	This work + IR results from DAVIES et al. (1985)
55.3462(55)	LIU and OKA (1985)
47.5	BUNKER et al. (1984)
72.	Ab initio calculation from BUNKER et al. (1983)
46.	Ab initio calculation from BOTSCHWINA et al. (1983)
28.2	Ab initio calculation from SPIRKO and BUNKER (1982)

TABLE II : Inversion splitting of the H_3O^+ ground state, in cm^{-1}.

Acknowledgments : This work was partially supported by the "Centre National de la Recherche Scientifique" (ATP 938-12) and by the "Etablissement Public Régional Nord - Pas-de-Calais". It has been made possible by the loan of the carcinotron from the "Centre Commun de Mesures de l'Université de Lille I". We are very grateful to T. OKA and P. DAVIES for sending us preprints on their works and to P.R. BUNKER for providing us unpublished predictions of the H_3O^+ energy levels. We are also greatly indebted to P. ROSSEELS for developing the phase lock system for the carcinotron and for his technical assistance.

References

BEGEMAN M.H., GUDEMAN C.S., PFAFF J. and SAYKALLY R.J. : Phys. Rev. Lett. 51, 554 (1983).
BOGEY M., DEMUYNCK C., DENIS M., DESTOMBES J.L. and LEMOINE B. : 1984a, Astron. Astrophys. 137, L15.
BOGEY M., DEMUYNCK C. and DESTOMBES J.L. : 1984 b, Astron. Astrophys. 138, L11.
BOGEY M., DEMUYNCK C., DESTOMBES J.L. and LAPAUW J.M.: 1985, to be published.
BOTSCHWINA P., ROSMUS P. and REINSCH E.A. : 1983, Chem. Phys. Lett. 102, 299.
BUNKER P.R., KRAEMER W.P. and SPIRKO V. : 1983, J. Mol. Spectrosc. 101, 180.
BUNKER P.R., AMANO T. and SPIRKO V. : 1984, J. Mol. Spectrosc. 107, 208.
BUNKER P.R. : 1985, private communication.
DALGARNO A. and BLACK J.H. : 1976, Rep. Progr. Phys. 39, 573.
DAVIES P.B., HAMILTON P.A. and JOHNSON S.A. : 1984, Astron. Astrophys. 141, L9.
DAVIES P.B., HAMILTON P.A. and JOHNSON S.A. : 1985, J. Opt. Soc. Amer., to be published.
DE LUCIA F.C., HERBST E., PLUMMER G.M. and BLAKE G.A. : 1983, J. Chem. Phys. 78, 2312.
GORDY W. and COOK R.L. : 1984, Microwave Molecular Spectra, J. Wiley and Sons Ed.
GRAEDEL R.E., LANGER W.D. and FRERKING M.A. : 1982, ApJ. Suppl. Ser. 48, 321.
HAESE M.N. and OKA T. : 1984, J. Chem. Phys. 80, 572.
LEMOINE B. and DESTOMBES J.L. : 1984, Chem. Phys. Lett. 111, 284.
LEUNG C.M., HERBST E. and HUEBNER W.F. : 1984, ApJ Suppl. Ser. 56, 231.
LIU D.J. and OKA T. : 1985, Phys. Rev. Lett. 54, 1786.
LIU D.J., HAESE M.N. and OKA T. : 1985, to be published.
PHILLIPS T.G., BLAKE G.A., KEENE J., WOODS R.C. and CHURCHWELL E. : 1985, to be published.
SMITH D. and ADAMS N.G., 1981, Int. Rev. Phys. Chem. 1, 271.
SCHWARZ H.A. : 1977, J. Chem. Phys. 67, 5525.
SPIRKO V. and BUNKER P.R. : 1982, J. Mol. Spectrosc. 95, 226.
WATSON W.D. : 1978, Ann. Rev. Astron. Astrophys. 16, 585.