A&A 441, 1039–1041 (2005)
DOI: 10.1051/0004-6361:20053260

Astronomy & Astrophysics

Laboratory measurement of the $J, K = 1, 0^- – 0, 0^+$ transition of ortho-D_3O^+

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Received 19 April 2005 / Accepted 17 May 2005

ABSTRACT

The $J, K = 1, 0^- - 0, 0^+$ transition of ortho-D_3O^+ was measured by laboratory submillimetre-wave spectroscopy using a source-modulated spectrometer combined with a hollow-cathode free-space cell. The D_3O^+ ion was generated by a dc glow discharge of D_2O. A single line, which showed characteristic behaviour of a molecular ion, was observed at exactly the frequency predicted by the molecular constants previously determined by Araki et al. (1999, Mol. Phys., 97, 177). The measured line frequency was corrected for the ion-drift Doppler shift and determined to be $798\,713.814 \pm 0.077$ MHz with one standard error of the measurements in parentheses. The lowest J, K transition of ortho-D_3O^+ can be used as a probe to investigate the ortho to para ratio or the ortho and para to meta ratio of interstellar D_3O^+ in highly depleted molecular cores.

Key words. molecular data – line: identification – ISM: molecules

1. Introduction

The recent detection of highly fractionated doubly deuterated ammonia with $[NHD_2]/[NH_3] = 0.005$ towards a dark cloud core L134N (Roueff et al. 2000) has prompted astronomical studies of multiply deuterated interstellar molecular species and stimulated chemical modelling of interstellar deuterium fractionation. Turner (1990) detected the first interstellar doubly deuterated formaldehyde in the compact ridge of Ori-KL and suggested a contribution from an active surface catalysis to deuterium fractionation in the region. In 2002 Lis et al. detected the ground state rotational transition $J_K = 1_0 \rightarrow 0_0(0a - 0s)$ of triply deuterated ammonia with $[ND_3]/[NH_3] = 0.0008$ in the Barnard 1 cloud. Almost concurrently van de Tak et al. (2002) observed the same transition towards the NGC 1333 region and reported the abundance ratio of 0.001 for $[ND_3]/[NH_3]$. Both results can be explained by means of gas-phase chemical models. Furthermore Parise et al. (2002, 2004) detected doubly and triply deuterated methanols, CHD_2OH and CD_3OH, in the solar type protostar IRAS 16293-2422 and reported that the abnormally high abundance ratios of 0.014 derived for $[CD_3OH]/[CH_3OH]$, 0.06 for $[CHD_2OH]/[CH_3OH]$, and 0.30 for $[CH_2DOH]/[CH_3OH]$ are consistent with a formation of methanol on grain surfaces with the high atomic D/H ratio of 0.1 to 0.3 in the accreting gas. Vastel et al. (2003) detected doubly deuterated hydrogen sulfide toward a sample of Class 0 sources and dense cores and supported also the grain surface chemistry for deuterium fractionation of H_2S. The high abundance ratios of these multiply deuterated species to their corresponding parent molecules are suggested to be due to the high depletion of C/O in the dense core (Brown & Millar 1989; Roberts & Millar 2000) or formation of molecular species on the grain surfaces (Tielens 1983). Caselli et al. (2003) recently detected a strong line of ortho-H_2D^+ at 372 GHz towards a prestellar core, L1544, confined within ~20″, where CO is highly depleted (Caselli et al. 1999). This firm observation of H_2D^+ validated the results of the depletion model. Roberts et al. (2003) showed that a significant enhancement of the fractionation of ionic and neutral species reported can be explained when all possible deuterated isotopomers of H_3^+ are included in interstellar deuterium chemistry. Very recently Vastel et al. (2004) detected the $1_{10}–1_{01}$ transition of D_2H^+ at 692 GHz toward the same prestellar core 16293E, encouraged by a laboratory measurement of the same transition (Hirao & Amano 2004). They concluded that the observed para-D_2H^+/ortho-H_2D^+ ratio is a verification of the model described above. Caselli (2002) carried out a detailed dynamical analysis of molecules, including deuterated species, in the prestellar cores and showed that the dominant molecular ion is H_3O^+ in the highly C/O depleted core.

The ν_3 infrared band of H_3O^+ was first observed by Begemann et al. (1983, 1985) using a colour center laser spectrometer combined with velocity modulation and the ν_2 band by Haese & Oka (1983) with a diode laser spectrometer. Since H_3O^+ is a pyramidal molecule showing approximately 55 cm^{-1} splitting due to inversion motion through the plane of the hydrogen atoms, it has only four submillimetre-wave transitions in the 300 GHz region. On the basis of the molecular constants determined by infrared studies, Plummer et al. (1985)

and Bogey et al. (1985) measured the four inversion rotation transitions of H_3O^+ in the laboratory. Verhoeve et al. (1989) extended measurements to the far-infrared region with FIR laser sideband spectroscopy and determined detailed molecular constants in both inversion states. Several inversion-rotational transitions of both ortho- and para- species of D_3O^+ were studied by submillimetre-wave spectroscopy and their inversion splitting was determined to be 15.36 cm^{-1} (Araki et al. 1998, 1999).

Interstellar detections of H_3O^+ have not been straightforward. In 1986 Hollis et al. reported detection of the $J, K = 1, 1^{-}-2, 1^{+}$ transition of para-H_3O^+ at 307 GHz towards Orion-KL and at the same time, Wootten et al. (1986) detected the same transition towards OMC-1 and Sgr B2. However, the observations were made for a single transition and were weak and disturbed by other strong lines. These detections had been considered to be preliminary and in 1991 Wootten et al. detected the $J, K = 3, 2^{+}-2, 2^{-}$ transition at 365 GHz again towards TMC-1 and Sgr B2. Furthermore, Phillips et al. (1992) studied three reasonably accessible low-lying submillimetre lines of H_3O^+ at 396, 365, and 307 GHz towards several giant molecular clouds including spectroscopically confused Orion-Kl and Sgr B2. They reported a clear detection of the 396 GHz line in the W3 IRS 5 source. This observation established the existence of H_3O^+ in space. The interstellar far-infrared emission line of H_3O^+, $J, K = 4, 3^{-}-3, 3^{+}$, was detected towards the shocked molecular hydrogen peak near Orion BN by Timmermann et al. (1996) using the Kuiper Airborne Observatory. Goicoechea & Cernicharo (2001) identified three far-infared absorption lines of both ortho- and para-H_3O^+ towards Sgr B2 and derived their column densities concluding the ortho to para ratio to be $\cong 1/(1.25 \pm 0.5)$.

2. Laboratory measurements

The $J, K = 1, 0^{-}-0, 0^{+}$ transition of D_3O^+ was measured at around 799 GHz using a submillimetre-wave spectrometer (Saito & Goto 1993) combined with a phase-locked Gunn oscillator source. The Gunn oscillator, giving an output power of 30–40 mW in a frequency range of 133–138 GHz, was used to drive a multiplier chain of a doubler and a tripler (Radiometer Physics) and an output power of about 100 μW was generated and used to measure spectral lines. The Gunn oscillator was phase-locked (XL Microwave) to an X-band microwave synthesizer whose frequency is scanned by sequential steps of about 0.2 kHz and to which tone-burst modulation of 500 kHz was applied (Pickett 1980). The signal was phase sensitively detected at a burst frequency of 96 kHz. The fully deuterated ion was generated in a free space absorption cell of 2 m in length by a hollow cathode discharge of D_2O. The $J, K = 1.0^{-}-0.0^{+}$ line was found exactly at the predicted frequency of 798 713.7 MHz (Araki et al. 1999) and it decreased by about half in intensity when 63 Gauss was applied to the cell (Saito et al. 1985). The observing conditions were a discharge current of 400 mA, a pressure of 3 Pa, and a temperature of 247 K. An example of the observed spectral line is shown in Fig. 1. The line frequency was determined from an average of five measurements: to be 798 713.954 (77) MHz where the value in parentheses indicates an experimental error in a unit of the last significant digit due to one standard deviation of five measured frequencies. The measured frequency includes an ion Doppler shift of 0.140 MHz (Araki et al. 1998) and, therefore, the corrected line frequency was determined be 798 713.814(77) MHz.

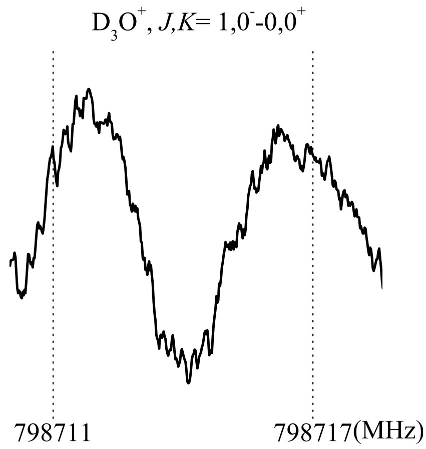

Fig. 1. The $J, K = 1, 0^{-}-0, 0^{+}$ transition of D_3O^+. The ion was produced by a 400 mA dc discharge of D_2O (3Pa) at a temperature of 247 K. The spectral range shown was observed with 220 s scan.

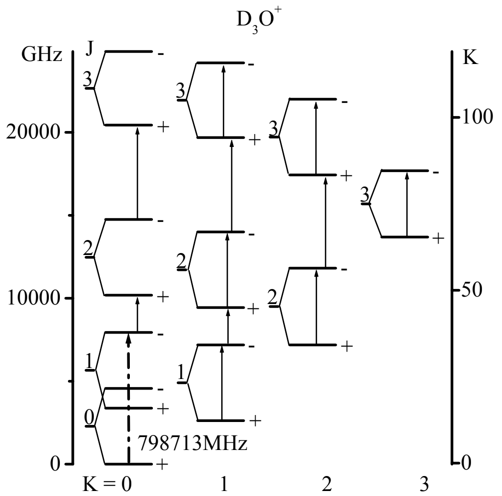

Fig. 2. Energy level diagram of D_3O^+ indicating the observed submillimetre-wave transitions with full upward lines.

3. Discussions

The observed frequency agrees well with the predicted frequency of 798 713.69(19) MHz within experimental error of limits. The predicted frequency was calculated from the molecular constants previously reported (Araki et al. 1999) and the error in parentheses corresponds to three standard errors due to experimental errors of the previously reported molecular constants. Figure 2 shows an energy level diagram of D_3O^+, which has C_{3v} symmetry like ND_3. The rotational levels of D_3O^+ in the symmetric (+) ground state of the inversion mode are classified as ortho for $K = 0$, $J = even$, para for $K = 0, J = odd$, ortho+para for $K = 3n$, and meta for $K = 3n \pm 1$. The ortho and para rotational levels in the antisymmetric (-) state are classified vice versa. Since a symmetric top such as ND_3 has its dipole moment along the symmetry axis, transitions between the ortho, meta and, para levels are strictly forbidden. Therefore, the $J, K = 1, 0^{-}–0, 0^{+}$ transition is the most fundamental line for the ortho species of interstellar D_3O^+ whereas the $J, K = 1, 1^{-}–1, 1^{+}$ transition is the fundamental line for the meta species as reported previously (Araki et al. 1999). The measured frequency of the $J, K = 1, 0^{-}–0, 0^{+}$ transition may be useful for the astronomical observation of ortho-D_3O^+ toward highly depleted cores.

Acknowledgements. The authors are grateful to H. Ozeki and M. Araki for their advice and help in the design of the Gunn oscillator system, and to I. K. Ahmad for her critical reading of the manuscript. The present study was supported by Grants-in-Aid from the Ministry of Education, Science, and Culture (No. 12440161).

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