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Letter to the Editor

Laboratory measurement of H_3O^+ line positions around 10 μm for astrophysical searches

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Summary

Several transitions of the $1^- \leftarrow 0^+$ infrared band of the H_3O^+ ion of interest in astronomy have been measured near the band centre at 10μm. The measurements are more accurate than earlier results and in very good agreement with the predicted spectrum.

Key words : Molecular ion, laboratory spectrum, infrared laser.

Introduction

Infrared laser heterodyne astronomy has yielded important information recently on both planetary and stellar environments (Betz, 1981; Rothermel et al., 1984). Infrared detection is particularly important for molecules without permanent electric dipole moments such as C_2H_4 and SiH_4. A prime region for their detection is around 10μm where N_2O and CO_2 lasers provide local oscillator frequencies. Although it had earlier been extensively studied by radioastronomy infrared detection of ammonia proved valuable for probing the ground state of the molecule (Betz and McLaren, 1980).

Isoelectronic with NH_3 is the ion H_3O^+ which has been postulated as a constituent of diffuse clouds where it could be formed via proton transfer with H_2O^+ (see the review by Smith and Adams, 1981). H_3O^+ has recently been detected in the laboratory by infrared laser spectroscopy (Begemann et al., 1983; Haese and Oka, 1984; Lemoine and Destombes 1984). The band of particular interest for heterodyne astronomical searches is the ν_2 mode, $1^- \leftarrow 0^+$ inversion component, centred at 10.5μm. A number of absorptions around the band centre were detected by Haese and Oka and calibrated against D_2CO lines to an accuracy of 0.005 cm^{-1}. Concurrently we have detected many more transitions in this band between 750 and 1170 cm^{-1}. Our lines are calibrated against accurately measured N_2O, CO_2, NH_3 and SO_2 lines, including laser transitions in N_2O and CO_2 where possible. This communication reports the measurement of several of the transitions expected to be intense in low temperature astronomical sources with the precision necessary for infrared astronomy.

Measurements

The source of H_3O^+ was a low pressure discharge in H_2/O_2 mixtures in a 1 m long 0.9 cm diameter water cooled tube. The transitions were detected using the velocity modulation technique introduced by Saykally and co-workers (Gudeman et al. 1983). For this purpose the discharge was driven by a high voltage transformer and power amplifier combination capable of delivering currents of up to 160 mA at 5 kHz. The highest S:N ratios observed in this band are over 100:1 with a 1 second time constant, while for lines in the $1^+ \leftarrow 0^-$ component at lower frequencies absorptions several times stronger have been detected. The calibration procedure involved sequential measurement of H_3O^+ line, calibrating gas line and germanium etalon. Although the H_3O^+ lines were broadened by modulation effects accurate location of the line centre with the large S:N ratios obtainable presented no difficulty. With many measurements of each line our estimated error is better than 0.001 cm^{-1}.

The principle source of error in the present work is frequency uncertainty caused by drift of the laser heat sink during and between scans. This dominates any possible systematic error due to thermal drift of the etalon, poor calibration line etc.. If a laser line is used for calibration it is unnecessary, in this experiment, to impress the laser transition onto the spectrum as an emission line since the technique is sufficiently sensitive to detect these transitions in a 50 cm long absorption cell. In the heterodyne method relatively close coincidence of local oscillator and molecular frequencies is required, usually well within 0.1 cm^{-1}. Therefore we have chosen to use (N_2O) laser lines for calibration only if they are close enough to warrant it, otherwise very accurate ammonia lines are used. The results of these measurements are given in table 1.

Table 1. Positions of H_3O^+ Transitions $1^- \leftarrow 0^+$ Band

Transition	*Calculated Relative Intensity	Position (cm^{-1}) Measured+	Position (cm^{-1}) Calculated	Calibration Line (cm^{-1})
P(1,0)	100	931.8968(7)	931.8976	932.082716 $^{14}N_2O$
Q(1,1)	100	953.9739(6)	953.9747	954.059628 $^{14}N_2O$
Q(2,2)	50	953.8071(6)	953.8072	953.82248 $^{14}NH_3$
Q(3,3)	20	953.8990(7)	953.8988	953.82248 $^{14}NH_3$
Q(4,4)	1	954.2509(6)	954.2508	954.34683 $^{14}NH_3$
Q(6,6)	-	955.7502(16)	955.7497	955.67666 $^{14}NH_3$
Q(7,7)	-	956.9083(13)	956.9078	956.84173 $^{14}NH_3$
Q(10,10)	-	962.1190(14)	962.1187	962.14439 $^{14}NH_3$
Q(11,11)	-	964.4707(11)	964.4717	964.461213 $^{14}N_2O$

* Calculated at 30K

+ Uncertainties are 2 standard deviations

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Results

The calculated positions are based on a much larger set of data containing (so far) 54 P, Q, and R transitions from this band. (The numerical results of the fit of this data will be published elsewhere). Agreement between calculated and measured positions is very satisfactory and of the order of the experimental uncertainty. The calculated absorption intensities for 30K are given in table 1. The Q(1,1) transition remains the strongest, apart from R(1,0), up to about 50K. The strongest absorption from 60 - 400K becomes the Q(3,3) component and from about 400 - 600K (and higher) the Q(6,6) transition. While the present measurements are some five times more accurate than those reported by Haese and Oka, further improvement by a factor of two or three should be possible by simultaneous recording of absorption and calibration line, and improvement in the temperature stability of the diode. Ultimately accurate location of the line centre will be limiting, and further improvement would require a laboratory heterodyne measurement.

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