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LABORATORY MILLIMETER AND SUBMILLIMETER SPECTRUM OF HOC^+

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ABSTRACT

The $J = 1 \rightarrow 2$, $2 \rightarrow 3$, and $3 \rightarrow 4$ rotational transitions of the molecular ion HOC^+ have been measured in the laboratory at frequencies from 178 to 358 GHz. Our data should permit astronomers to confirm the recent possible sighting of the $J = 1 \rightarrow 0$ transition of HOC^+ in Sgr B2 at 89.5 GHz.

Subject headings: interstellar: molecules — laboratory spectra

Based on the laboratory detection of HOC^+ by Gudeman and Woods (1982), Woods *et al.* (1982) have recently observed and tentatively identified a weak emission line in Sgr B2 as the $J = 1 \rightarrow 0$ transition of HOC^+. Assuming the correctness of the identification, Woods *et al.* (1982) obtained an HCO^+/HOC^+ abundance ratio of ~ 330 and used a model consisting of ~ 20 ion-molecule reactions to deduce that the large abundance ratio implies the existence of a significant abundance of H I in dense interstellar clouds. In this *Letter*, we report the laboratory measurement of three additional rotational transitions of HOC^+. These transitions, with rotational quantum numbers $J = 1 \rightarrow 2$, $2 \rightarrow 3$, and $3 \rightarrow 4$, lie in the millimeter and submillimeter regions of the electromagnetic spectrum and help confirm the laboratory identification of HOC^+. The $J = 2 \rightarrow 3$ and $3 \rightarrow 4$ lines, at 268.5 and 357.9 GHz, respectively, should be observable by astronomers. Interstellar observation of HOC^+ at higher frequencies would confirm the identification of this species in Sgr B2 by Woods *et al.* (1982).

Our millimeter and submillimeter spectroscopic techniques have been discussed previously (De Lucia 1976). The HOC^+ ion was produced in a 5 foot long, 1.5 inch diameter discharge cell at liquid N_2 temperature that was covered by a solenoid to produce axial magnetic fields of up to 200 gauss. A discharge current of 10 mA was maintained at a voltage of 5 kV. The total pressure in the cell was 10 mtorr, and the chief constituent was argon, with trace amounts of H_2 and CO (Gudeman and Woods 1982). The magnetic field enhanced the signals sufficiently to permit detection of HOC^+ with lock-in signal recovery at a time constant of 1 s. We have previously discussed the large enhancement in signal attainable via magnetic confinement of molecular ions such as NO^+, HCO^+, etc. (Bowman, Herbst, and De Lucia 1982).

The transition frequencies measured in this experiment are listed in Table 1. These frequencies have been corrected for a small but unusual Doppler shift in the following manner. The $J = 2 \rightarrow 3$ transition was observed with both relative directions of the microwave beam and the ion drift velocity by placing the detector at different ends of the cell. It was found that the net direction of ion flow was *opposite* to the sense expected from the polarity of the electrodes. Presumably, this effect was caused by the vacuum pump operating on a small-diameter discharge tube.

The rotational constants B_0 and D_0 obtained from a least squares fit to the data are also listed in Table 1. These constants permit accurate calculation of rest frequencies for a wide range of transitions. For the $J = 0 \rightarrow 1$ transition, we predict a frequency of 89,487.387(28) MHz, in good agreement with the value of 89,487.414(15)

TABLE 1

MEASURED ROTATIONAL TRANSITIONS OF HOC^+ (MHz)

Transition $J'' \rightarrow J'$	Observed[a]	Obs. − Calc.[b]
$1 \rightarrow 2$	178972.051	0.034
$2 \rightarrow 3$	268451.094	−0.038
$3 \rightarrow 4$	357921.987	0.012

[a] Includes shift to cancel Doppler effect caused by ion drift velocity and vacuum pump.

[b] Fitted constants are B_0 = 44,743.9235(140) MHz and D_0 = 114.89(54) kHz.

MHz obtained by Gudeman and Woods (1982). As expected (Gudeman and Woods 1982), the centrifugal distortion constant, D_0, of HOC^+ is significantly larger than that of HCO^+.

The analysis of the observed HCO^+/HOC^+ abundance ratio in Sgr B2 by Woods *et al.* (1982) leads to the conclusion that the relative weakness of the signal ascribed to HOC^+ is due primarily to the selective depletion reaction, $HOC^+ + H \rightarrow H + OCH.^+$ An atomic hydrogen abundance considerably greater than the CO abundance appears to be required, which is in conflict with ion-molecule model predictions. Basic to the analysis is the assumption that the reaction between CO and H_3^+ produces equal amounts of HCO^+ and HOC^+. While this may be true, it is in conflict with the phase space theory of reaction collisions (Light 1967) which predicts the more exothermic pathway ($HCO^+ + H_2$) to be dominant. In addition, recent experimental work by Illies, Jarrold, and Bowers (1982) on collision-induced dissociation patterns indicates that the reaction between H_3^+ and CO produces between 2% and 10% $HOC^+ + H_2$. If we utilize the 2% figure, then an HCO^+/HOC^+ abundance ratio of ~ 50 can be caused by the difference in production rates, and the abundance of atomic hydrogen need not be as large as required by Woods *et al.* (1982).

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