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NSG 7105

INDIRECT OBSERVATION OF UNOBSERVABLE INTERSTELLAR MOLECULES

(NASA-CR-149870) INDIRECT OBSERVATION OF UNOBSERVABLE INTERSTELLAR MOLECULES (NASA) 41 p HC A03/MF A01 CSCL 03A
N77-19964
Unclas
G3/89 21702

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ABSTRACT

It is suggested that the abundances of neutral non-polar interstellar molecules unobservable by radioastronomy can be systematically determined by radio observation of the protonated ions. As an example, observed N_2H^+ column densities are analyzed to infer molecular nitrogen abundances in dense interstellar clouds. The chemistries and expected densities of the protonated ions of O_2, C_2, CO_2, C_2H_2 and CH_4 are then discussed. Microwave transition frequencies for HCO_2^+ and $C_2H_3^+$ are estimated, and a preliminary astronomical search for HCO_2^+ is described.

I. INTRODUCTION

The discovery of an intricate interstellar chemistry has been almost entirely an achievement of radio astronomy. Large, high density clouds--the regions where molecules exist in appreciable abundance--are optically opaque; it is therefore important for an understanding of the chemistry of the interstellar medium to rely on radio observations and to extend these to new classes of molecules. In this paper, we shall explore the feasibility of determining by indirect means the abundances of non-polar neutral species which are not in themselves directly observable by radio techniques. We are especially interested in species such as N_2, O_2, C_2, CO_2, C_2H_2, and CH_4, all of which may be present to an appreciable extent in dense interstellar clouds. In addition, we are interested in an indirect determination of the H_2O abundance because the amount of water present cannot be obtained from the maser transition observed. It is necessary to determine the abundances of all of these species if the chemistry of dense clouds is every to be fully understood.

An abundance for any species can be obtained theoretically from a model of molecule formation and depletion if that model is complete with respect to all processes that affect the species of interest to an appreciable extent. (See for example, Herbst and Klemperer 1973, hereafter abbreviated as HK). In this paper, a much less complete analysis is utilized. In particular, we examine the abundances of the protonated polar ions N_2H^+, O_2H^+, C_2H^+, $HOCO^+$, H_3O^+, $C_2H_3^+$, and CH_5^+ predicted relative to their neutral precursors. It is assumed that these ionic species are produced and destroyed by gas phase ion-molecule and ion-electron reactions. The rate coefficients of the relevant reactions are frequently known from laboratory measurements with high accuracy (10-20%) and in general may be approximated by simple theoretical techniques (HK). For exothermic ion-molecule reactions, the rate coefficient is almost always near the Langevin value of 2×10^{-9} cm^3 sec^{-1} whereas for ion-electron dissociative recombination reactions, the rate coefficient is usually $\sim$ 1-2 $\times 10^{-6}$ cm^3 sec^{-1} (HK). From the appropriate kinetic equations, it is possible to deduce abundance ratios between the protonated ions and their neutral precursors. Then, a direct measurement of the protonated ion abundance leads to an indirect determination of the neutral abundance. A neutral abundance obtained by our analysis is ideally dependent on the following assumptions only:

1) a cosmic ray induced ionization rate

2) the occurrence of rapid exothermic ion-molecule reactions at interstellar cloud temperatures.

However, the neutral densities we obtain are partially model dependent because certain results of the HK gas phase model (e.g., electron densities) must sometimes be utilized. Note that the possiblity of reaction on grain surfaces has not been excluded in this paper.

The motivation for this paper comes from the observation of HCO^+ by Buhl and Snyder (1970), and Snyder et al. (1975) plus that of N_2H^+ by Turner (1974), and Thaddeus and Turner (1975). These observations demonstrate that polyatomic ions exist in appreciable abundance in the interstellar medium and that, consequently, ion-molecule reactions must occur. Until recently, identification of interstellar HCO^+ and N_2H^+, being based on theoretical arguments, (e.g., Green et al. 1974) had been regarded by some as equivocal. The recent success of Woods et al. (1975) in observing the microwave spectra of these two ions in the laboratory has confirmed their interstellar identification. In addition, the laboratory technique of Woods et al. (1975; see also Saykally et al. 1976) promises to aid astronomers greatly in their search for a richer variety of interstellar molecular ions.

Since N_2H^+ has now been unambiguously identified in interstellar clouds, our method can be applied quantitatively to the abundance of molecular nitrogen. It is deduced that N_2 is probably the major nitrogen species in dense clouds. This point is noteworthy in view of the failure to observe N_2 in diffuse clouds with the Copernicus satellite (Snow 1975). For the other important neutral species, O_2, C_2, CO_2, H_2O, C_2H_2, CH_4, observation of the protonated species has not yet been achieved in either the laboratory or interstellar clouds. In this paper estimates for the rotational transition frequencies of some of these ions are provided along with discussions of their probable column densities. It is to be hoped that highly accurate experimental frequencies of some of the ions discussed here will soon become available so that extensive searches for the protonated species of unobservable neutrals can be undertaken.

II. DIATOMIC SPECIES

a) N_2

To determine the molecular nitrogen abundance from the observed N_2H^+ column density, it is necessary to consider the ion-molecule chemistry relating to N_2 and N_2H^+. Table 1 shows the relevant reactions together with their rate constants. It is assumed that CO is much more abundant than CO_2 and H_2O. If these latter molecules are, on the contrary, as abundant or even more abundant than CO, more reactions must be considered in the analysis. However, the inferred N_2 abundance is sensitive only to the sum of CO, CO_2, and H_2O concentrations, and is virtually independent of their relative abundances. Dissociative recombination of N_2H^+ with electrons is ignored in our analysis. If the CO concentration reflects a strongly depeted carbon elemental abundance rather than the normal cosmic abundance ratio assumed in HK, and if the electron abundance is an order of magnitude higher than the HK values, then electron-ion recombination cannot be ignored.

We cannot make the assumption that N_2H^+ comes from N_2 because of the likelihood that reactions such as $NH_3^+ + N = N_2H^+ + H_2$ occur. However, we can obtain a lower limit to the molecular nitrogen density by assuming that the <u>only</u> mechanism for N_2 formation involves N_2H^+ and CO (both unambiguously observed species): $N_2H^+ + CO \rightarrow HCO^+ + N_2$. Once formed, N_2 is almost an inert species, reacting with no neutrals known to be present in abundance. Molecular nitrogen does react with the ions H_3^+ and He^+, formed via cosmic ray bombardment (Table I). The steady-state assumption applied to N_2[1] leads

to the relation (valid if $[N_2] << [CO]$)

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[1] Assumption of the standard grain parameters leads to the conclusion that the ion-controlled depletion rate of N_2 is probably slower than the maximum condensation rate on grains. If we assume that the N_2 absorbed on grains is unreactive, then the only effect of such a depletion process is to transfer some of the gas phase N_2 onto the grains.

$$\frac{[N_2]}{[CO]^2} \geq \frac{k_3}{k_{4a}\, k_{1a}/k_{5a} + 0.28\, k_{4b}\, k_{1b}/k_{5b}} \frac{[N_2H^+]}{[H_2]} \quad (1)$$

where the cosmic abundance of helium is set equal to 0.14 of the hydrogen abundance (Allen 1973). The symbol "[ ]" stands for density and the k_i refer to the appropriate rate coefficients. Turner (1974) has estimated that in the clouds he observed $[N_2H^+]/[H_2] \approx 3 \times 10^{-11}$ with an order of magnitude uncertainty. For the CO density in relation (1), it is reasonable to substitute the cosmic abundance of carbon multiplied by twice the H_2 density (HK). Then, for a "typical" dense cloud in which $[H_2] \sim 10^4$ cm^{-3}, the inferred nitrogen density is $[N_2] \geq 0.1$ cm^{-3}. An upper limit to the N_2 density is given by cosmic abundance considerations (HK); viz., $[N_2] \leq 1$ cm^{-3}. Similarly, for a cloud with $[H_2] = 3 \times 10^4$ cm^{-3}, 1 $cm^{-3} \leq [N_2] \leq 3$ cm^{-3}. It is doubtful that higher density regions were sampled by Turner (1974). Snyder (1975) has reported an observation of diminishing N_2H^+ density towards the denser regions of Orion A, but detailed numerical figures are not yet available. The proximity of the lower and upper limits to the N_2 concentration is strong evidence that, at the least, a significant fraction of the nitrogen cosmic abundance exists in the form of N_2 in clouds of density $n \geq 10^4$ cm^{-3}. This conclusion also obtains in the full HK model. If a significant portion of the carbon were depleted from the gas phase, the quantitative but not the qualitative conclusions of this analysis would have to be modified.

It is interesting to speculate on the atomic vs. molecular fraction of the nitrogen abundance. The intensity of the observed N_2H^+ emission apparently suggests via the above analysis, that to within an order of magnitude all nitrogen is in the diatomic form. (The observed concentration of ammonia is too small to be of significance in this discussion.) Yet, the uncertainties in both observation and analysis certainly do not preclude the statement that atomic nitrogen may be of equal or even greater abundance than N_2. Indeed, the existence of cosmic ray-produced helium ions will always serve to produce some N from N_2 (Farragher 1970, Laudenslager et al. 1974): $N_2 + He^+ \rightarrow N^+ + N + He$. Thus, only in regions (if they exist) sufficiently dense to exclude 100 MeV cosmic rays is it feasible to neglect atomic nitrogen.

b) O_2

Several groups have studied the kinetics of the reaction $H_3^+ + O_2 \rightleftarrows O_2H^+ + H_2$ (Fehsenfeld, Lindinger, and Albritten 1975; Kim, Beard, and Huntress 1976). It appears that the reactants and products are isoenergetic. At 298°K, both the forward and reverse reactions are rapid with K, the equilibrium constant, near unity. . . In addition, the forward and reverse rate coefficients are virtually independent of energy. It therefore must be tentatively concluded that $K \approx 1.$ at interstellar cloud temperatures. Because depletion by reaction with molecular hydrogen is so efficient, no other depletion mechanisms need be considered for O_2H^+. There are no other important formation mechanisms than the one mentioned above. Therefore, at steady state,

$$[O_2H^+] = [H_3^+] \frac{[O_2]}{[H_2]} \approx \frac{k_1}{k_5} \frac{[O_2]}{[CO]} \qquad (2)$$

To obtain a severe upper limit to the O_2H^+ density, assume that $[O_2] \approx [CO]$. Then $[O_2H^+] < 1.0 \times 10^{-8}$ cm^{-3}. For a cloud of dimension 10^{19} cm, we can expect a maximum O_2H^+ column density of 1.0×10^{11} cm^{-2}, well below the sensitivity limit of current observational technique. Thus, our method cannot yet be utilized as an indirect means of O_2 detection. In general, any ion that reacts rapidly with H_2 will have an abundance too low to be measured at this time.

c) C_2

The formation of C_2 in interstellar clouds of moderate density has been discussed by Solomon and Klemperer (1972). The reaction of C_2 with H_3^+ to give C_2H^+ is exothermic and is assumed to be rapid. C_2H^+ can also be formed via the sequence of reactions:

$$C^+ + CH \rightarrow C_2^+ + H$$

$$C_2^+ + H_2 \rightarrow C_2H^+ + H.$$

Unfortunately, analogous to the case of O_2 discussed above, C_2H^+ cannot be used to monitor the C_2 abundance since it reacts rapidly with H_2 forming $C_2H_2^+$, and the equilibrium abundance of C_2H^+ is therefore expected to be too low to detect (Kim, Beard, and Huntress 1975). In fact, this reaction sequence terminates with dissociative recombination of $C_2H_2^+$ to give C_2H, a known interstellar molecule (Tucker, Kutner, and Thaddeus 1974).

III. TRIATOMIC SPECIES

a) CO_2

The molecular ion $HOCO^+$ is formed and depleted principally by those reactions shown in Table 2. The steady-state abundance of $HOCO^+$ is then

$$[HOCO^+] = \left\{\frac{k_6[H_3{}^+] + k_7[N_2H^+]}{k_8}\right\} \frac{[CO_2]}{[CO]}. \qquad (3)$$

Reaction (8) has not been investigated experimentally. If it were unexpectedly slow, or if CO were not the dominant non-hydrogenic neutral species, other depletion mechanisms for $HOCO^+$ might gain importance; viz.,

$HOCO^+ + H_2O \rightarrow H_3O^+ + CO_2$

$HOCO^+ + O \rightarrow HCO^+ + O_2$

$HOCO^+ + N \rightarrow HCO^+ + NO$

$HOCO^+ + e \rightarrow CO_2 + H.$

If these $HOCO^+$ reactions with neutrals occur as expected at the normal Langevin rate, inclusion of species such as H_2O, O_2, and N in the analysis would only affect the result to the extent that CO in Eq. (3) would have to be replaced by the sum of several densities. If $[CO_2]$ and $[N_2]$, as expected, are << [CO], Eq. (3) simplifies to

$$\frac{[CO_2]}{[CO]^2} \approx \frac{k_{5a}k_8}{k_{1a}k_6}\,\frac{[HOCO^+]}{[H_2]} \approx 7.7 \times 10^7\,\frac{[HOCO^+]}{[H_2]} \qquad (4)$$

Green et al. (1976) have recently calculated the electronic structure and equilibrium geometry of $HOCO^+$. According to their calculation, the structure is that of a slightly asymmetric prolate top, with the rotational constants listed in Table 3; also listed in this table are the predicted frequencies of several a-type microwave transitions betweem low-lying ($k_{-1} = 0$) rotational levels. These rotation constants and transition frequencies are reasonably insensitive to minor adjustments in the equilibrium geometry, and the uncertainties quoted in Table 3, which are slightly less than 1%, are hopefully conservative.

The asymmetrical geometry of $HOCO^+$ has an interesting virtue from an astronomical standpoint: it endows the rotational spectrum with a specificity not found in a linear molecule, and makes an astronomical search worthwhile even in the absence of precise line frequencies. Consider for example the $J = 4-3$ transition, which is of interest because it will probably be stronger in space than the other lines in Table 3, and because it happens to lie in a part of the spectrum where extremely sensitive receivers currently exist. In addition to the $K_{-1} = 0$ transition listed in Table 3, there are nearby in frequency three K-type doublets corresponding to $K_{-1} = 1$, 2, and 3. The upper levels of these transitions lie respectively 44, 144, and 310 K above the rotational ground state, so these transitions will definitely be excited in comparatively hot molecular clouds like Ori A.

This rotational structure constitutes a highly distinctive fingerprint for $HOCO^+$. The $K_{-1} = 1$ doublet is widely split, by $4(B_o - C_o) \approx 650$ MHz; its center of gravity will fall near, but (because of centrifugal distortion) not precisely on the $K_{-1} = 0$ line. To judge from the centrifugal distortion parameters of the similar molecules HNCO and HN_3, the centrifugal shift of the center of gravity should be about 6 MHz to lower frequency. The $K_{-1} = 2$ doublet, on the other hand, is expected to be barely resolved:

the calculated splitting is 0.28 MHz, which is at the limit of resolution in a very narrow line source like OMC-2; the center of gravity of this doublet is expected to be centrifugally shifted about 24 MHz to lower frequency. Finally, the $K_{-1} = 3$ doublet will be totally unresolved, and is expected to be shifted about 54 MHz to lower frequency. It is clear that even if some of these lines could be detected enough information would be available to almost certainly identify the $HOCO^+$ molecule.

With these considerations in mind, we have attempted to find $HOCO^+$ with the NRAO 36-foot telescope*. Two of the best molecular sources, Ori A and DR21(OH), were systematically surveyed in frequency over a range which exceeded the uncertainty in the J = 4-3 transition according to Table 3 (the equally good source Sgr B2 was unfortunately too near the sun at the time of this survey to be observed). In particular, the frequency region 83.25 to 87.05 GHz was surveyed in Ori A, and the region 80.40 to 86.875 was

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*The National Radio Astronomy Observatory is operated by Associated Universities, Inc., under contract to the National Science Foundation.

surveyed in DR21(OH). No lines were detected in either source which could be attributed to $HOCO^+$. A uniform upper limit cannot be precisely set because the sensitivity of the search was somewhat different at different frequencies, but it is probably safe to conclude that any $HOCO^+$ line stronger than 0.5K (radiation temperature) would have been picked up in either source.

This upper limit can in turn be converted into interesting upper limits on the CO_2 abundance and the CO_2/CO ratio. It will be assumed that the observational limit refers to the $K_{-1} = 0$ transition i.e., the transition $4_{04}-3_{03}$, and we will confine our attention to Ori A. For an optically thin line of radiation intensity T_R, the column density is

$$N_{HOCO^+} = \frac{8\pi\nu^2 \ \Delta v k T_R}{hc^3 A f} , \qquad (5)$$

where $A = 1.31 \times 10^{-5}$ sec $^{-1}$ is the Einstein coefficient of the 4_{04} level calculated from the <u>ab initio</u> value of 2 D for the permanent electric dipole moment along the OCO axis (Green et al. 1976), and f is the fractional population of the 4_{04} level. A reasonable lower limit on f is 0.05, based on the excitation of molecules similar to $HOCO^+$ in Ori A. Then taking $\Delta v = 4$ km sec^{-1} for the linewidth in Ori A (the observed linewidth of HCO^+), and $T_R \lesssim 0.5$ K, we find from Eq. (4) that

$$N_{HOCO^+} \lesssim 4 \times 10^{13} \ cm^{-2}. \tag{6}$$

The Ori A source in HCO^+ and other ions is probably $\sim 10^{18}$ cm in the line of sight, so for a mean $HOCO^+$ density we find

$$[HOCO^+] \lesssim 4 \times 10^{-5}. \tag{7}$$

Finally, via Eq. (4) it is possible to set a crude upper limit on the CO_2/CO ratio in Ori A. Taking as reasonable values for this source $[CO] \approx 10 \ cm^{-3}$, $N_{H_2} \approx 2 \times 10^{23} \ cm^{-2}$, and assuming that the density ratio of $HOCO^+$ to H_2 is equal to the ratio of corresponding column densities, we find that,

$$[CO_2]/[CO] \lesssim 0.15 \tag{8}$$

Current notions of the formation of CO_2 in molecular clouds are too vague to warrant much discussion of this limit. It is to be hoped that the $HOCO^+$ frequencies will soon be refined by laboratory measurements so that more stringent astrophysical searches can be performed.

b) H_2O

The recent observation of the isotopic species HDO (Turner et al. 1975) implies that H_2O is present in large abundance in dense clouds. Observation of the H_3O^+ (oxonium) ion would permit another, perhaps more precise, determination of the H_2O abundance. The oxonium ion is expected to be one of the most abundant molecular ions (HK). It is ioselectronic with ammonia and should possess a similar inversion-rotation spectrum. Novick, Stevens, and Klemperer (1975) have performed an ab initio calculation of the H_3O^+ inversion potential. These authors estimate an inversion frequency of 84 cm^{-1}, unlike the 24 GHz NH_3 inversion frequency. If this calculation is correct, H_3O^+ posses no transitions favorable to microwave detection.

The observation of HDO (Turner et al. 1975) in the Kleinmann-Low nebula ($[H_2] \sim 10^7$ cm^{-3}), mentioned above, leads to speculation that gaseous H_2O consumes much of the oxygen abundance in dense clouds. This possibility can probably be excluded for most HCO^+ sources. Our reasoning is as follows: if H_2O were present in "appreciable" abundance (e.g., $[H_2O] \approx [CO]$), HCO^+ would be depleted by the reaction,

$$HCO^+ + H_2O \rightarrow H_3O^+ + CO$$

more efficiently than by the sole HK mechanism,

$$HCO^+ + e \rightarrow CO + H.$$

The result would be that HCO^+ would lose its position as the dominant polyatomic ion and be reduced to a column density no larger than that of other ions such as N_2H^+. However, in almost all sources except Orion A, HCO^+ is thought to be considerably more abundant than N_2H^+ (Turner 1975). We therefore conclude tentatively that in all likelihood, H_2O is not as abundant a species as CO in dense clouds.

IV. POLYATOMIC SPECIES

a) C_2H_2

Table IV contains the ion-molecule chemistry of the vinyl cation $C_2H_3^+$. It is assumed that protonation of acetylene (C_2H_2) occurs predominantly via reaction with HCO^+. The vinyl cation is not depleted by reaction with abundant CO, but is probably depleted by reaction with such species as O, N, O_2, and H_2O as well as by electron recombination. The assumption that $C_2H_3{}^+$ is at steady-state leads to the relation

$$[C_2H_2] = \left\{k_{10}[e] + k_{11}\,[H_2O] + k_{12}[O] + k_{13}[N] + k_{14}[O_2]\right\} \frac{[C_2H_3{}^+]}{[HCO^+]} \qquad (9)$$

The acetylene abundance can therefore be estimated from knowledge of the vinyl cation to HCO^+ abundance ratio. To perform this estimation, we assume that,

$$[H_2O] + [O] + [N] + [O_2] \approx 2 \times 10^{-4}\,[H_2]\,.$$

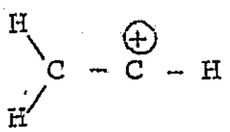
This assumption is based on HK estimates but can be defended on simple cosmic abundance arguments. The dissociative electron recombination contribution to $C_2H_3{}^+$ depletion can probably be ignored in a rough analysis unless electron abundances are somewhat higher than currently estimated. With these simplifications, relation (9) reduces to

$$\frac{[C_2H_2]}{[H_2]} \approx 2 \times 10^{-4} \frac{[C_2H_3^+]}{[HCO^+]} . \tag{10}$$

HCO^+ column densities are not known because of unknown opacities but $N_{HCO^+} \approx 10^{14-15}$ cm^{-2} is a reasonable estimate (Turner 1975). A measurement of $N_{C_2H_3^+} \approx 10^{13}$cm^{-2} would then imply that $[C_2H_2]/[H_2] \approx 2 \times 10^{-5} - 2 \times 10^{-6}$.
It should be noted that the vinyl cation cannot be produced from C_2H because $C_2H_2^+$, the protonated ion of C_2H, does not react with H_2 to form $C_2H_3^+$ (Kim, Beard, and Huntress 1975). Therefore, $C_2H_3^+$ is an indicator of acetylene density only.

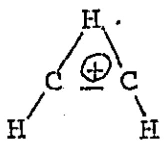
The structure of the vinyl cation has been studied theoretically by several groups (Hariharan, Lathan, and Pople 1972; Zurawski, Ahlrichs, and Kutzelnigg 1973; and Weber et al. 1976). There are two possible structures of similar energy:

(a)



or

(b)



and it is unclear which geometry possesses the greater stability, although the most reliable calculations seem to favor structure (b). Structures (a) and (b) are both slightly asymmetric prolate tops. Structure (b) permits only strong b-type transitions at frequencies in the far infrared, whereas structure (a) allows $\Delta K = 0$ and K-doubling a-type transitions. A recent calculation (Weber et al. 1976) indicates that the barrier against tunneling between the two structures is only 500 - 1500°K. If this range of values is correct, such a motion would have to be considered in an analysis of the expected spectra. If interstellar detection of the vinyl cation is to be accomplished with current microwave receivers, structure (a) will have to be thermally populated at low temperature. Table V lists the rotational constants for (a) as well as several rotational transition frequencies. Error estimates are uncertain but are at least ±1 GHz for the $\Delta J = 1$ transitions.

b) CH_4

The abundance of methane in dense interstellar clouds is of great interest. Is gas phase carbon mostly in oxidized species such as CO and CO_2 or is a high percentage tied up in saturated hydrocarbons such as CH_4? Observation of CH_5^+ might help to elucidate this problem. There exist a number of theoretical studies of the structure of this ion (Lathan, Hehre, and Pople 1971 ; Hariharan, Lathan, and Pople 1972; Dyczmons, Staemmler, and Kutzelnigg 1970). Several structures--of C_{4v}, D_{3h} and C_s symmetry--have been investigated. Of these, the asymmetric C_s structure appears to be the lowest in energy by less than 1 eV. Guest, Murrell, and Pedley (1971) found the potential surface of CH_5^+ to be extremely flat at the C_s equilibrium geometry. These authors also determined that two of the hydrogens could undergo virtually free rotation. The expected microwave spectrum of such a poorly defined structure with large amplitude motion is difficult to deduce. Much more theoretical work is needed.

V. OTHER IONS OF IMPORTANCE

In the preceeding section, the observation of protonated ionic species has been discussed as a means of obtaining information about unobservable neutrals. There are other ions which are of interest to an understanding of interstellar cloud chemistry for a variety of reasons. Two of these species merit special concern.

The ion H_2CN^+ is thought to be a precursor of HCN (HK, Watson 1974, Herbst 1976). There is reason to believe that the HK model underestimated the abundance of this ion. Pearson and Schaefer (1974) have performed ab inition calculations on $HCNH^+$ and have deduced a linear structure with $B_o = 37.4$ GHz. The uncertainty in the prediction of the $J = 1 \rightarrow 0$ transition, lying at 74.8 GHz, is probably less than 1 GHz, and may be as small as 300 MHz.

Herbst (1976) has suggested that the ion $H_2CNH_2{}^+$ can be formed by an especially favorable radiative association process,

$$H_2CN^+ + H_2 \rightarrow H_2CNH_2{}^+ + h\nu .$$

Methylenimmonium ($H_2CNH_2{}^+$) can then recombine dissociatively to form H_2CNH (methanimine) or add another H_2 via radiative association. Observation of $H_2CNH_2{}^+$ (especially coupled with observation of $HCNH^+$) could test this hypothesis. Kollman et al. (1973) have calculated a structure for H_2CNH^+. (See Table VI.) Based on this structure, we have computed the rotational constants of this slightly asymmetric prolate top and tabluated several rotational transition frequencies of interest (Table VI). As is the case for $C_2H_3^+$, the uncertainty in the frequencies of the $\Delta J = 1$ lines is likely to be at least ± 1 GHz.

VI. DISCUSSION

In this paper we have considered an indirect method for the determination of molecules that are normally unobservable under interstellar conditions. The ion-molecule kinetics and rotational spectra of the protonated ions of N_2, O_2, CO_2, H_2O, C_2H_2 and CH_4 have been discussed. Since laboratory microwave absorption spectra of ions has been demonstrated by Woods, our estimates of transition frequencies hopefully will be replaced by measurements. Of considerable importance in understanding the molecular composition of the interstellar medium is the <u>active</u> oxygen to carbon ratio. If indeed most molecular formation occurs in the gas phase, then the O/C ratio in that phase should be reflected by the molecular composition observed by radio astronomy. In this article we have suggested that present observations show both H_2O and CO_2 are much less abundant than CO. We note that CO_2 is the expected form of excess oxygen, from equilibrium considerations. In particular the reaction $CO_2 + H_2 = CO + H_2O$ is endothermic by 0.5 ev.

The conclusion that CO_2 and H_2O are considerably less abundant than CO suggests that the gas component of the interstellar medium is more strongly depleted with respect to oxygen than carbon. This conclusion is based primarily on observations in dense clouds. The Copernicus observations, which are direct, have sufficient uncertainty that it is not possible to establish the O/C gas phase ratio usefully in diffuse clouds. The high fraction of atomic oxygen (O^I) and atomic carbon (C^I and C^{II}) in diffuse clouds implies that the molecular abundances therein will not be seriously affected by the O/C ratio.

The presence of molecular nitrogen is established by the abundance of N_2H^+. The important question of the relative ratio of N_2/N cannot be well answered by N_2H^+ alone.

We have received a manuscript of a very relevant article by Snyder, Hollis and Watson, "An Interpretation of the Anomalous Variation of $N_2H^+/HCO/SO_2$ in Orion: Support for Ion-Molecule Reactions". This article establishes limits on the abundance of H_2O in agreement with the results discussed here.

ACKNOWLEDGMENTS

E. H. wishes to thank the Faculty Research Committee of the College of William and Mary for a summer research grant. S. G. acknowledges support from NASA under Grant No. NSG 7105.

TABLE I

Major Ion-Molecule Reactions Involving N_2H^+ and N_2

Reaction	Rate Coefficient(k)	Reference
1 a) H_2 + C.R. Proton → H_2^+ + e + C.R.P.'	0.95×10^{-17} s^{-1}	Herbst & Klemperer 1973
b) He + C.R. Proton → He^+ + e + C.R.P.'	1.0×10^{-17} s^{-1}	
2 $H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1×10^{-9} cm^3 s^{-1}	Bowers et al. 1969
3 $N_2H^+ + CO \rightarrow HCO^+ + N_2$	8.8×10^{-10} cm^{3}s^{-1}	Herbst et al. 1975
4 a) $N_2 + H_3^+ \rightarrow N_2H^+ + H_2$	1.8×10^{-9} cm^{3}s^{-1}	Bohme et al. 1973
	1.7×10^{-9} cm^{3}s^{-1}	Kim et al. 1976
b) $N_2 + He^+ \rightarrow$ Products	1.2×10^{-9} cm^{3}s^{-1}	Farragher 1970 Laudenslager et al. 1974
5 a) $CO + H_3^+ \rightarrow HCO^+ + H_2$	1.4×10^{-9} cm^{3}s^{-1}	Burt et al. 1970
	1.7×10^{-9} cm^{3}s^{-1}	Kim et al. 1976
b) $CO + He^+ \rightarrow C^+ + O + He$	1.7×10^{-9} cm^{3}s^{-1}	Fehsenfeld et al. 1966
	1.6×10^{-9} cm^{3}s^{-1}	Laudenslager et al. 1974

TABLE II

Major Ion-Molecule Reactions Concerning $HOCO^+$

	Reaction	Rate Coefficient	Reference
6	$CO_2 + H_3^+ \rightarrow HOCO^+ + H_2$	$1.9 \times 10^{-9} cm^3 \ s^{-1}$	Burt et al. 1970
7	$CO_2 + N_2H^+ \rightarrow HOCO^+ + N_2$	$9.2 \times 10^{-10} cm^3 \ s^{-1}$	Burt et al. 1970
8	$HOCO^+ + CO \rightarrow HCO^+ + CO_2$	$1 \times 10^{-9} cm^3 \ s^{-1}$	Estimate

TABLE III

$HOCO^+$

A) Rotational Constants (MHz) [good to better than 1%]

A_o = 706,000

B_o = 10,820

C_o = 10,660

$b_p = -\ 1.15 \times 10^{-4}$

B) Rotational Transition Frequencies

J'	K'_{-1}	k'_1	J"	$K"_{-1}$	$K"_1$	υ (MHz)
1	0	1	0	0	0	21,480 ± 200
2	0	2	1	0	1	42,960 ± 400
3	0	3	2	0	2	64,440 ± 600
4	0	4	3	0	3	85,920 ± 800

TABLE IV

Major Ion-Molecule Reactions Concerning $C_2H_3^+$

Reaction	Rate Coefficient	Reference
9 $C_2H_2 + HCO^+ \rightarrow C_2H_3^+ + CO$	$2 \times 10^{-9} cm^3\ s^{-1}$	Estimate
10 $C_2H_3^+ + e \rightarrow$ Products	$2 \times 10^{-6} cm^3\ s^{-1}$	Herbst and Klemperer 1973
11 $C_2H_3^+ + H_2O \rightarrow C_2H_2 + H_3O^+$	$1.11 \times 10^{-9} cm^3\ s^{-1}$	Huntress (1976)
12 $C_2H_3^+ + O \rightarrow H_2C_2O^+ + H$	$2 \times 10^{-9} cm^3\ s^{-1}$	Estimate
13 $C_2H_3^+ + N \rightarrow H_2C_2N^+ + H$	$2 \times 10^{-9} cm^3\ s^{-1}$	Estimate
14 $C_2H_3^+ + O_2 \rightarrow C_2H_2O_2^+ + H$	$2 \times 10^{-9} cm^3\ s^{-1}$	Estimate

TABLE V

H_2CCH^+ (Vinyl Cation)

A) Rotational Constants (MHz)

A_o = 282,000

B_o = 33,250

C_o = 29,750

$b_p = -7 \times 10^{-3}$

B) Rotational Transition Frequencies

J'	K'_{-1}	K'_1	J''	K''_{-1}	K'_1	ν (MHz)
1	0	1	0	0	0	63,000
2	0	2	1	0	1	126,000
1	1	0	1	1	1	3,500
2	1	1	2	1	2	10,500

TABLE VI

$H_2CNH_2^+$ (Methylenimmonium)

A) Rotational Constants (MHz)

$A_o = 152{,}000$

$B_o = 29{,}900$

$C_o = 25{,}000$

$b_p = -.02$

B) Rotational Transition Frequencies

J'	K'_{-1}	K'_1	J''	K''_{-1}	K''_1	υ (MHz)
1	0	1	0	0	0	54,900
2	0	2	1	0	1	109,700
1	1	0	1	1	1	4,900
2	1	1	2	1	2	14,700

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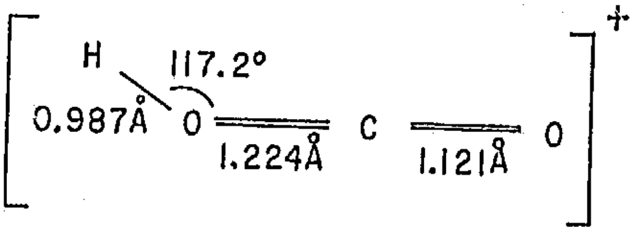

Fig. 1

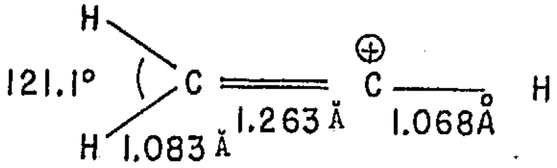

Fig. 2

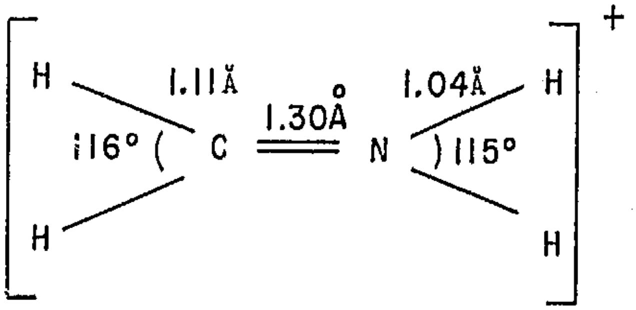

Fig. 3

FIGURE CAPTIONS

Fig. 1 Calculated Structure of $HOCO^+$ from Green et al. (1976).

Fig. 2 Structure of $H_2C_2H^+$ (vinyl cation) computed by Hariharan et al. (1972).

Fig. 3 Structure of $H_2CNH_2^+$ (Methylenimmonium) computed by Kollman et al. (1973).