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ESTIMATES OF N_2 ABUNDANCES IN DENSE MOLECULAR CLOUDS

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ABSTRACT

Interstellar N_2 abundances toward 13 dark clouds and warm star-forming regions are derived from column densities measured for N_2H^+. The N_2H^+ abundances were determined from a millimeter-wavelength study of the molecule's $J = 1 \rightarrow 0$ and $J = 3 \rightarrow 2$ rotational transitions, as well as from observations of the $^{15}NNH^+$ and $N^{15}NH^+$ isotopic spectra. Abundances of N_2 were estimated from N_2H^+ assuming the chemistry had achieved steady state. Fractional abundances of N_2 with respect to H_2 are typically $f \sim 3 \times 10^{-6}$ for eight warm clouds and $f \sim 6 \times 10^{-6}$ for four cold clouds, with an average value of $f \sim 4 \times 10^{-6}$. These abundances are in good agreement with predictions of ion-molecule models of interstellar chemistry in quiescent clouds which have reached steady state. The relatively high N_2 concentrations suggest that the most of the nitrogen in dense clouds is in the form of molecular nitrogen. Given that the N_2 abundances are comparable in both warm and cold clouds, condensation onto grains may not play a large role in the nitrogen chemistry of dense gas.

Subject headings: ISM: abundances — ISM: clouds — ISM: molecules — molecular processes

1. INTRODUCTION

Nitrogen is the fifth most abundant element in the universe and is thought to be mainly in the form of N and N_2 in most astronomical sources. In dense gas, ion-molecule models of interstellar chemistry predict N_2 to be the primary carrier of nitrogen. However, due to its symmetric nature, N_2 has no permanent electric dipole moment and, hence, possesses no pure rotational spectrum. Therefore, N_2 cannot be directly observed in molecular clouds using radio- or millimeter-wavelength techniques. N_2 also has no electronic transitions in the optical region, and vibrational transitions of the molecule are not likely to be observed in dense clouds, where kinetic temperatures typically do not exceed 500 K. Furthermore, $^{15}N^{14}N$ has a very small dipole moment ($< 10^{-2} D$), and the pure rotational spectrum of this isotopic species has never been measured in the laboratory. Moreover, no electronic transitions of species containing the N_2 bond, such as N_2^+, have been observed in interstellar optical spectra. Consequently, the N_2 abundance in interstellar clouds has not been observationally established, although it is thought to be an extremely important sink for elemental nitrogen.

The amount of N_2 in molecular clouds, however, can be measured indirectly through millimeter-wavelength observations of its protonated form, N_2H^+. The major route to formation of N_2H^+ in dense clouds is the ion-molecule reaction

$$N_2 + H_3^+ \rightarrow N_2H^+ + H_2 , \qquad (1)$$

which proceeds at the rate $k_1 = 1.3 \times 10^{-9}$ cm^3 s^{-1}, measured at 30 K (Marquette, Rebrion, & Rowe 1989). Although H_3^+ has no permanent dipole moment, and thus has not been detected in the interstellar medium, it is considered to be one of the most abundant ions in an astrophysical plasma. It is thought to be produced by cosmic-ray ionization of H_2 (e.g., Brown & Rice 1986). Virtually all interstellar N_2H^+ is considered to be produced from the reaction (1) and destroyed primarily by the dissociative electron recombination reaction,

$$N_2H^+ + e^- \rightarrow N_2 + H , \qquad (2)$$

which has a rate coeffient $k_2 = 1.6 \times 10^{-3}$ cm^3 s^{-1} measured at 110 K (Amano 1990). Because N_2 is involved in both production and destruction of N_2H^+, the abundance of the ion is a direct reflection of the amount of N_2 present in a cloud. Thus, by accurately establishing abundances of N_2H^+, it is possible to make a reasonable estimate of the abundances of N_2 (e.g., Herbst et al. 1977). Unfortunately, N_2H^+ has not been a very well-studied molecule, and hence column densities of this important species were, in general, poorly known.

Very recently, however, a detailed survey of N_2H^+ was carried out toward both warm and cold molecular clouds (Womack, Ziurys, & Wyckoff 1992). Column densities of this ion were established by observing both the $J = 1 \rightarrow 0$ and $J = 3 \rightarrow 2$ rotational transitions of N_2H^+ as well as by measuring the $^{15}NNH^+$ and $N^{15}NH^+$ isotopic lines, and by using a large velocity gradient (LVG) analysis. The abundances of N_2H^+ in dense gas are now well established and can be used to determine those of N_2. In this paper, we estimate N_2 abundances from N_2H^+ column densities and then compare them with chemical models of dense clouds. Implications of these abundances with nitrogen chemistry are also discussed.

2. DERIVING N_2 ABUNDANCES FROM N_2H^+ DATA

The survey of the $J = 1 \rightarrow 0$ and $J = 3 \rightarrow 2$ rotational transitions of N_2H^+ as well as the $J = 1 \rightarrow 0$ transition of $^{15}NNH^+$ and $N^{15}NH^+$ was performed in 1990 April toward several warm and cold dense clouds using the NRAO 12 m telescope[5] telescope (Womack et al. 1992). Column densities for N_2H^+ were calculated both analytically and with an LVG analysis, modeling the two rotational transitions observed. The N_2H^+ emission was found to be generally optically thin, as determined from the ^{15}N isotope observations. Fractional abundances of N_2H^+, relative to molecular hydrogen, were

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calculated using H_2 column densities from the literature, obtained from both CO and dust continuum observations.

The N_2H^+ ion was found to exhibit very narrow line profiles ($\Delta v_{1/2} \sim$ 1–5 km s^{-1}) and to have low excitation temperatures ($T_{ex} < 30$ K). There was no evidence in any of the spectra that N_2H^+ arises from hot, perturbed gas. Thus, N_2H^+ mainly traces the relatively cool, quiescent gas of dense clouds. Abundances of N_2 established from the ion therefore apply to cooler, unperturbed extended gas.

While most observed molecular abundances in dense gas are reproduced fairly well by ion-molecule models processed the equivalent of only $\sim 10^5$ yr or at "early times," the N_2H^+ abundances measured in the survey are better predicted by models of clouds processed the equivalent of $\sim 10^6$ yr, or when "steady state" is reached (Brown & Rice 1986; Millar 1990; Herbst & Leung 1989). It is therefore likely that N_2H^+ is observed primarily in quiescent gas where the chemistry has achieved steady state (Womack et al. 1992).

For gas in which a steady state chemistry is reached, the formation and destruction mechanisms of molecules are balanced. In this circumstance $d[N_2H^+]/dt = 0$, and the following relationship between the abundances of N_2 and N_2H^+ can be derived from equations (1) and (2),

$$[N_2] = [N_2H^+] \frac{[e^-]k_2}{[H_3^+]k_1}, \quad (3)$$

where $[e^-]$ and $[H_3^+]$ are the electron and H_3^+ concentrations, respectively. The abundance of N_2 can thus be obtained from that of N_2H^+, and the relationship between $[e^-]$ and $[H_3^+]$, provided the steady state condition is applied.

Establishing the relationship between $[e^-]$ and $[H_3^+]$ is not trivial. To a first-order approximation $[e^-] \sim [H_3^+]$ (Watson 1976). However, recent ion-molecule models suggest a somewhat different ratio. For example, Herbst & Leung (1989) and Brown & Rice (1986) predict $[e^-]/[H_3^+] \sim 10$, while Langer & Graedel (1989) and Millar (1990) suggest $[e^-]/[H_3^+] \sim 20$. In view of this, we have estimated the electron density to be approximately an order of magnitude higher than the H_3^+ density in the quiescent gas of dense clouds.

Specification of a more precise relative abundance of $[e^-]$ and $[H_3^+]$ is difficult. Recent measurements of the H_3^+ dissociative electron recombination rate suggest a rate constant much lower than previous values, which would increase the amount of H_3^+ in dense clouds (Smith & Adams 1984). This would lower the $[e^-]/[H_3^+]$ ratio in the models above. Even more recent measurements indicate a recombination rate constant closer to earlier theoretical results (Amano 1988) indicative of a larger $[e^-]/[H_3^+]$ ratio. Hence the relative abundance of electrons and H_3^+ in dense clouds remains uncertain. Here we have adopted the simple assumption that $[e^-] \sim 10[H_3^+]$.

The next most important destruction mechanism of N_2H^+ after electron dissociative recombination is probably the reaction

$$N_2H^+ + CO \rightarrow N_2 + HCO^+ , \quad (4)$$

which proceeds at the rate 8.8×10^{-10} cm^3 s^{-1} for a temperature of 300 K (Herbst et al. 1975). Despite the low reaction rate, the high abundance of CO in dense clouds may make this reaction competitive with electron dissociative recombination. In fact, model predictions of CO and H_3^+ abundances (Herbst & Leung 1989; Langer & Graedel 1989; Millar 1990) suggest that this destruction pathway is comparable to that of electron dissociative recombination. If the CO abundance is very high, the destruction route (4) would increase the N_2 abundances at most by about a factor of 2 over the estimates presented here. Therefore, to a first approximation, electron dissociative recombination can be considered the major destruction mechanism for N_2H^+.

3. N_2 ABUNDANCES IN DENSE CLOUDS

Fractional abundances of N_2 toward 13 galactic clouds derived from N_2H^+ data as discussed in the previous section are presented in Table 1. Included in the table are the column densities of N_2H^+ and H_2 used in the analysis. As is seen from the table, there is little difference between the N_2 abundances toward the warm and cold clouds. For the warm star-forming regions, $f \sim 3 \times 10^{-6}$, and for the cold clouds L134 N, TMC-1, Orion(3N,1E), and ρ Oph, the N_2 abundances are slightly higher, $f \sim 6 \times 10^{-6}$. A mean fractional N_2 abundance for both warm and cold clouds of $f = (4 \pm 3) \times 10^{-6}$ is derived, where the error represents the dispersion about the unweighted mean.

The lowest fractional abundance of N_2, $f \sim 5 \times 10^{-8}$, was found toward one region of ρ Oph, a system of dark molecular clouds containing several dense cores. A comparison of our source position with mapping data of CO (Loren & Wootten 1986) indicates that the N_2H^+ spectrum from which the N_2 abundance was calculated, was obtained at the outer edges of the complex. Spectra of N_2H^+ obtained directly toward a nearby (5′ W) massive core (Loren & Wootten 1986) show emission approximately ~ 20 times stronger than the data obtained at the cloud edge. This suggests that there may be significant variations in N_2H^+ (and N_2) abundance from the central to the outer regions of ρ Oph.

An upper limit of $f < 10^{-6}$ was calculated for the N_2 abundance toward B335. Spectra of CO in the region (Frerking, Langer, & Wilson 1987) indicate that $n(H_2) \lesssim 1000$ cm^{-3} at our source position. This low cloud density is probably not sufficient to excite N_2H^+, which has a high electric dipole moment (3.4*D*), and may be the reason the molecule was not detected at this position.

Toward Sgr B2N and Sgr B2(OH) several differing velocity components were observed in the N_2H^+ $J = 1 \rightarrow 0$ and $J = 3 \rightarrow 2$ spectra, making it difficult to calculate N_2H^+ column densities toward these sources. Because of the complicated line profiles, column densities were calculated analytically from the $J = 0$ transition only using the optically thin approximation (see Womack et al. 1992). Because the $J = 1 \rightarrow 0$ line may be optically thick, the N_2H^+ column densities, and consequently the N_2 abundances of $f \sim 5 \times 10^{-7}$ toward Sgr B2N and 4×10^{-7} toward Sgr B2(OH), are likely to be underestimated.

The uncertainties of the N_2H^+ and H_2 column densities are approximately $\sim 50\%$ each. Hence, the N_2H^+ fractional abundances, from which the N_2 abundances are derived, are probably accurate to a factor of 2. Therefore, considering the uncertainties in $[e^-]$, $[H_3^+]$ and reaction rate coefficients, the N_2 abundances presented here are expected to have an error no greater than a factor of 10.

4. IMPLICATIONS FOR NITROGEN CHEMISTRY

4.1. *Nitrogen Chemistry and Steady State Models*

In contrast with oxygen- and carbon-containing species, chemical models of the nitrogen-bearing molecules in the inter-

TABLE 1

N_2 ABUNDANCES TOWARD WARM AND COLD CLOUDS[a]

Source	α (1950.0)	δ (1950.0)	$N(N_2H^+)$ (cm^{-2})	$N(H_2)$ (cm^{-2})	$f(N_2)$
1. W3(OH)	$2^h23^m17\overset{s}{.}0$	61°38′53″	2×10^{13}	1×10^{23}[b]	8×10^{-7}
2. TMC-1[a]	4 38 20.3	25 42 00	7×10^{12}	1×10^{22}[c]	9×10^{-6}
3. Orion-S	5 32 45.4	−05 26 05	3×10^{13}	1×10^{23}[d]	3×10^{-6}
4. Orion-KL	5 32 46.7	−05 24 23	1×10^{14}	7×10^{23}[e]	3×10^{-6}
5. Orion(3N, 1E)[a]	5 33 02.0	−05 21 20	6×10^{12}	1×10^{22}[c]	7×10^{-6}
6. L134 N[a]	15 51 30.0	−02 43 31	5×10^{12}	8×10^{21}[f]	8×10^{-6}
7. ρ Oph[a]	16 23 55.0	−24 15 49	7×10^{11}	2×10^{23}[g]	5×10^{-8}
8. Sgr B2N	17 44 09.5	−28 21 20	4×10^{13}	1×10^{24}[h]	5×10^{-7}
Sgr B2(OH)	17 44 11.0	−28 22 30	3×10^{13}	1×10^{24}[h]	4×10^{-7}
9. W49	19 07 51.3	09 01 20	2×10^{13}	1×10^{24}[i]	3×10^{-7}
10. W51 N	19 21 22.2	14 25 17	2×10^{14}	1×10^{24}[i]	3×10^{-6}
W51 M	19 21 26.3	14 24 37	1×10^{15}	1×10^{24}[i]	1×10^{-5}
11. B335[a]	19 34 54.0	07 27 20	$<1 \times 10^{11}$	1×10^{21}[j]	$<1 \times 10^{-6}$
12. DR21(OH)	20 37 13.8	42 11 53	5×10^{13}	1×10^{23}[k]	6×10^{-6}
13. NGC 7538	23 11 36.7	61 10 47	3×10^{13}	9×10^{22}[l]	4×10^{-6}
NGC 7538 IRS 1	23 11 36.0	61 11 47	3×10^{13}	9×10^{22}[l]	4×10^{-6}
NGC 7538 IRS 11	23 11 36.1	61 10 30	2×10^{13}	9×10^{22}[l]	3×10^{-6}

[a] Cold cloud ($T_K \sim$ 10–15 K)
[b] Guilloteau et al. 1983.
[c] Irvine et al. 1985.
[d] Ziurys et al. 1990.
[e] Plambeck et al. 1982.
[f] Swade 1989.
[g] Loren & Wootten 1986.
[h] Ziurys et al. 1991.
[i] Jaffee, Becklin, & Hildebrand 1984.
[j] Frerking et al. 1987.
[k] Richardson et al. 1986.
[l] Wilson et al. 1983.

stellar medium have not been constrained significantly by observations. This is because virtually no relevant observations have been made. Many basic nitrogen reactions and reaction rate coefficients also remain uncertain. In particular, the reactions which introduce nitrogen into the ion-molecule chemistry of interstellar clouds are poorly understood. Nitrogen chemistry is considered to be initiated by neutral-neutral reactions with low activation energies (Pineau des Forêts, & Flower 1990). Molecular nitrogen is generally thought to be initially produced from atomic nitrogen by the following reactions

$$N + OH \rightarrow NO + H\ , \tag{5}$$

and

$$N + NO \rightarrow N_2 + O\ . \tag{6}$$

Most ion-molecule models predict N_2 fractional abundances to be $f \sim 10^{-5}$ for both low- and high-metal steady state chemistry, and to be somewhat lower, $10^{-7} < f < 10^{-6}$, for both low- and high-metal early-time chemistry (Langer & Graedel 1989; Millar 1990; Herbst & Leung 1986, 1989; Pineau des Forêts et al. 1990; Brown & Rice 1986). It is important to note that all of the models discussed here predict N_2 abundances only for dark clouds, where $T_K \sim$ 10–20 K and $n(H_2) \sim (1\text{–}5) \times 10^4\ cm^{-3}$.

Comparison of model results with the derived N_2 abundances in Table 1 shows that the N_2 abundances toward the dark clouds TMC-1, L134 N, and Orion(3N, 1E) ($f \sim 8 \times 10^{-6}$) are in good agreement with the steady state values. Toward the warmer clouds, the N_2 abundances are slightly lower, $f \sim 3 \times 10^{-6}$, and are closer to the early-time predictions. However, within the estimated errors, the warm cloud N_2 abundances overlap the steady state values. Furthermore, as noted above, the models discussed here address only dark cloud N_2 abundances. Ion-molecule models of regions with $T_K \sim$ 50–100 K and $n(H_2) \sim 10^5\text{–}10^6\ cm^{-3}$ are needed to make a more accurate analysis of the N_2 abundances in the warm star-forming regions presented here. Ion-molecule models predict that N_2H^+ abundances (from which the amount of N_2 is estimated) should decrease with increasing temperature and density. Thus, the lower N_2 abundances derived toward the warm clouds may be indicative of the chemistry in the warmer and denser gas.

It appears that, to an order of magnitude, the derived N_2 abundances are in good accord with ion-molecule model predictions of dense clouds with steady state chemistry. Since the steady state assumption was used in estimating N_2 abundances from equation (3), this agreement suggests that there is consistency among the assumptions used. Observed N_2H^+ and NH_3 abundances are also better predicted by steady state ion-molecule models. Therefore, the steady state approximation may be appropriate for nitrogen chemistry in dense, quiescent gas, in contrast with most carbon- and oxygen-bearing species (Millar 1990).

It is interesting that while the dense cloud abundances of N_2H^+, N_2, and NH_3 are well reproduced by ion-molecule models of steady state chemistry, those of NO are better predicted by early-time values (Ziurys et al. 1991). The differences between the model predictions of N_2, N_2H^+, and NO is particularly interesting because of the related formation pathways. The production of NO in dense clouds is thought to be primarily from reaction (5). Molecular nitrogen can then be produced via reaction (6) from which N_2H^+ is thought to form. The direct link between the N_2, N_2H^+, and NO production suggests that the abundances of these four molecules should be predicted best by the same type of ion-molecule chemical model. Thus, it is difficult to understand why NO abundances are better fitted by early-time models, while N_2H^+ and N_2 abundances indicate that a steady state model is more appropriate.

Another set of reactions, initiated by carbon-bearing rather than oxygen-bearing molecules, has been suggested for the production of N_2H^+ (Nejad, Williams, & Charnley 1990). In this model, the following sequence

$$\mathrm{CH} + \mathrm{N} \rightarrow \mathrm{CN} + \mathrm{H}\,, \qquad (7)$$

$$\mathrm{CN} + \mathrm{N} \rightarrow \mathrm{N_2} + \mathrm{C}\,, \qquad (8)$$

is considered to be the most important route to N_2 formation. Perhaps the agreement of N_2H^+ and N_2 abundances with steady state models is due to a nitrogen chemistry initiated by reactions with carbon-based species, as opposed to the usual assumption of oxygen-based molecules as precursors. If nitrogen chemistry is indeed initiated by reactions involving carbon-based species, then one might expect the relative abundances of N_2H^+ (and N_2) to be very different in the clouds TMC-1 and L134 N, since TMC-1 has much higher abundances of carbon-rich molecules. Interestingly, the N_2 abundance toward TMC-1 (9×10^{-6}) is approximately the same as that measured toward L134 N (8×10^{-6}).

4.2. N_2: *The Most Abundant* N-*Bearing Molecule in Dense Clouds*

The relatively high N_2 abundances indicate that, in dense clouds, nitrogen is predominantly channeled into N_2. For example, the average fractional abundance of N_2, $f \sim 4 \times 10^{-6}$, is orders of magnitude larger than the observed abundances of other nitrogen-bearing species: $f(\mathrm{NH_3}) \sim 5 \times 10^{-8}$ (cf. Millar 1990), $f(\mathrm{NO}) \sim 8 \times 10^{-9}$ (Ziurys et al. 1991), $f(\mathrm{N_2H^+}) \sim 5 \times 10^{-10}$ (Womack et al. 1992), $f(\mathrm{CN}) \sim 1 \times 10^{-8}$ (Churchwell & Bieging 1983), $f(\mathrm{HCN}) \sim 1 \times 10^{-8}$ (Irvine & Schloerb 1984), and $f(\mathrm{HC_3N}) \sim 5 \times 10^{-10}$ (Swade 1989). The molecules NS and HNO have been conclusively detected only toward Sgr B2, and thus are not likely to be major carriers of interstellar nitrogen (Gottlieb et al. 1975; Hollis, Snyder, & Ziurys 1992). Furthermore, ion-molecule models predict that other nitrogen-bearing molecules which have not yet been observed in dense clouds, such as OCN, to have fractional abundances lower than $\sim 1 \times 10^{-7}$ (e.g., Herbst & Leung 1989; Chièze, Pineau des Forêts, & Herbst 1991). Thus, N_2 appears to be the dominant carrier of nitrogen in dense clouds.

It is interesting that N_2 appears to be the major nitrogen-bearing molecule, since it is composed of two N atoms. Because hydrogen is far more cosmically abundant than nitrogen, one might expect that the most prevalent nitrogen carrier would be a molecule composed of one nitrogen atom and hydrogen, such as NH_3. This does not appear to be the case. The large abundance of interstellar N_2 may be a result of the molecule's high stability; the species is closed-shell and contains a triple bond, similar to CO. In comparison, O_2 is a stable, homonuclear diatomic molecule that might be an important carrier of oxygen. Studies of $^{16}O^{18}O$ by Goldsmith et al. (1985) and Liszt & Vanden Bout (1985) have set limits to this species' abundance which are somewhat inconclusive. If O_2 is similar to N_2 then one might expect a substantial fraction of oxygen to be in the molecular form.

4.3. N_2 *and Interstellar Grains: No Depletion?*

In deriving the N_2 fractional abundance in dense molecular clouds, condensation of the species onto interstellar dust grains has been ignored. Loss of N_2 from the gas phase has consequently not been considered. It is worth examining whether a significant fraction of the elemental interstellar nitrogen could be locked up in grains. The temperature at which N_2 could condense into grains is low ($\sim$20 K, e.g., Lewis & Prinn 1980). If grain depletion were significant for N_2, and the gas and grain temperatures were coupled, then the fractional abundances of this molecule should be much lower in the cold clouds (with kinetic temperatures of $T_K \sim 10$ K) than in the warmer clouds ($T_K = 50$–100 K). However, no such effect is observed in the sources studied here. As Table 1 shows, there is not a significant difference between the fractional abundances of N_2 in the warm and the cold clouds. In fact, the N_2 abundances in L134 N, TMC-1, and Orion(3N, 1E) are slightly higher ($f \sim 8 \times 10^{-6}$) than those found in the warmer regions ($f \sim 3 \times 10^{-6}$).

The lack of effect of grain condensation on N_2 is interesting. The condensation temperature of N_2 is at a critical value which lies between the typical kinetic temperatures of the sample of cold and warm clouds studied here. Yet there appears to be no loss of N_2 out of gas phase in 10 K clouds versus 50 K objects. Condensation of N_2 onto grains, therefore, may depend on factors other than simply temperature, such as chemical surface effects.

5. CONCLUSIONS

Under the assumption that the quiescent gas in dense clouds has achieved a steady state chemistry, fractional abundances of N_2 in a sample of dense molecular clouds were established. These values were derived from N_2H^+ observations. The N_2 abundances were found to be $f \sim 4 \times 10^{-6}$ with a small dispersion about the mean. No significant differences were found between the amount of N_2 in dark and in warm clouds, which suggests that interstellar grains may not play an important role in the N_2 production (or depletion) in dense gas. The relatively high abundances found suggest that N_2 is probably the dominant nitrogen-bearing species in dense clouds.

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