

CHLORINE IN DENSE INTERSTELLAR CLOUDS: THE ABUNDANCE OF HCl IN OMC-1

GEOFFREY A. BLAKE,¹ JOCELYN KEENE,² AND T. G. PHILLIPS²

Received 1984 December 19; accepted 1985 February 25

ABSTRACT

We report the first detection of a chlorine-bearing molecular species in the interstellar medium via emission from the $J = 1 \rightarrow 0$ transition of HCl at 625.9 GHz toward OMC-1. The relative strengths, widths, and velocities of the resolved hyperfine components are consistent with moderate optical depth emission originating from dense, quiescent molecular cloud material ($V_{\text{LSR}} = 9 \text{ km s}^{-1}$). The overall emission strength implies a fractional abundance of $f(\text{HCl}/\text{H}_2) \sim (0.5\text{--}5.0) \times 10^{-8}$, depending on the density of the emitting region. This is approximately an order of magnitude below previous theoretical estimates and a factor of 3–30 below the cosmic abundance of Cl. Recent laboratory work suggests that the lowered fractional abundance of HCl is caused by a combination of depletion onto grains with gas-phase loss processes such as the reaction of HCl with C^+ .

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

Because of the large rotational energy level spacings and dipole moments of simple hydrides, their rotational line emission is a potentially large source of energy loss from collapsing molecular clouds, even for molecules with small fractional abundances. A particularly interesting example of this is given by hydrogen chloride. If all of the available chlorine were in the form of HCl in dense clouds ($f(\text{HCl}/\text{H}_2) \sim 1 \times 10^{-7}$), as suggested by early analyses of chlorine chemistry (Jura 1974; Dalgarno *et al.* 1974), then the cooling rates from HCl and CO emission would be equal within a factor of 2 for densities above 10^5 cm^{-3} even though HCl must be at least 2 orders of magnitude less abundant than CO (Dalgarno *et al.* 1974). Observations of hydrogen chloride should therefore provide information about both the abundance and distribution of a new element in molecular clouds as well as the nature of energy-balance processes within these objects. The large rotational constants of HCl place its pure rotational transitions in the submillimeter and far-infrared wavelength regions, which have only recently become accessible to observation.

As Figure 1 shows, the spin $3/2$ of the ^{35}Cl nucleus splits the rotational transitions of HCl into several hyperfine components, which, because of the large chlorine quadrupole moment, will be resolvable in many molecular clouds, possibly allowing approximate optical depths to be estimated without observing several different rotational states. The $\Delta F = \Delta J$ transitions are most strongly allowed in the classical (high- J) limit, but the low- J value involved in the ground-state transition places approximately 50% of the line strength into the $\Delta F = 0$ and $\Delta F = -\Delta J$ hyperfine satellites, as Figure 1 shows. The hyperfine splittings have been exaggerated in this figure for clarity.

We report here the first detection of interstellar HCl at any wavelength through observations of the ground-state $J = 1 \rightarrow 0$ transition centered at $625.9188 \pm 0.0001 \text{ GHz}$ (De Lucia, Helminger, and Gordy 1971) in OMC-1. Hydrogen chloride is also the first chlorine-bearing molecule detected in the interstellar medium. The relatively weak emission detected

here, coupled with the nondetection of HCl toward several diffuse clouds using optical techniques (Jura and York 1978; Wright and Morton 1979), suggests the need for a reexamination of the models previously used to describe interstellar chlorine chemistry.

II. OBSERVATIONS

Because of the high atmospheric opacity at $479 \mu\text{m}$, the wavelength of the ground-state rotational transition of HCl,

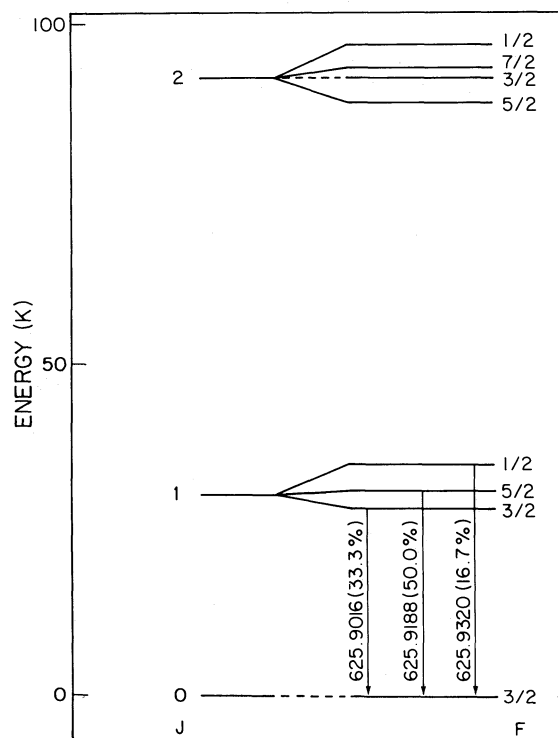


FIG. 1.—Energy-level diagram for the lowest three rotational levels of HCl, with the hyperfine splittings exaggerated for clarity. Arrows mark the observed transitions, with their laboratory rest frequencies shown also. The intrinsic line strengths are shown in parentheses.

¹ Department of Chemistry, California Institute of Technology.

² Department of Physics, California Institute of Technology.

these observations were performed on 1984 February 22 with NASA's Kuiper Airborne Observatory, flying at an altitude of 12.5 km. An InSb hot-electron bolometer heterodyne receiver similar to that described by Phillips and Jefferts (1974) served as the front end. Intermediate frequency filtering produced a single-channel instrument of 0.48 km s^{-1} (1.0 MHz) resolution, with spectra taken by sweeping the klystron local oscillator under computer control in 1 km s^{-1} intervals. The measured receiver temperature was $\sim 600 \text{ K}$.

The center of OMC-1 was observed by alternating integrations on the source with observations of two positions located $\pm 12'$ in azimuth from the source; integrations lasted about 1.5 minutes at each position. The total integration time was ~ 2 hours. At $479 \mu\text{m}$ the diffraction-limited beam size of the 0.91 m telescope is approximately $2'$ FWHM, while our estimated absolute pointing accuracy is $\pm 40''$.

Our antenna temperature scale was calibrated with observations of 290 and 80 K loads to determine the receiver temperature and with maps of the Moon, which was fully illuminated during the observations, to determine the beam efficiency for spatially extended sources. With assumed values of 97% for the lunar submillimeter emissivity (Linsky 1973) and 390 K for the temperature of the subsolar point, our measured beam efficiency was 46%. No planets were available to determine the aperture efficiency, but from previous airborne measurements at 492 and 572 GHz we estimate that it is about 30%.

III. RESULTS

Figure 2 shows the $J = 1 \rightarrow 0$ emission detected toward the center of OMC-1. The data points are spaced by 1 km s^{-1} , but have been Hanning smoothed to an effective velocity resolution of 2 km s^{-1} . The vertical bars indicate the positions of the three hyperfine components assuming a line central velocity of 9 km s^{-1} , while their heights indicate the relative strengths expected for thermalized optically thin emission.

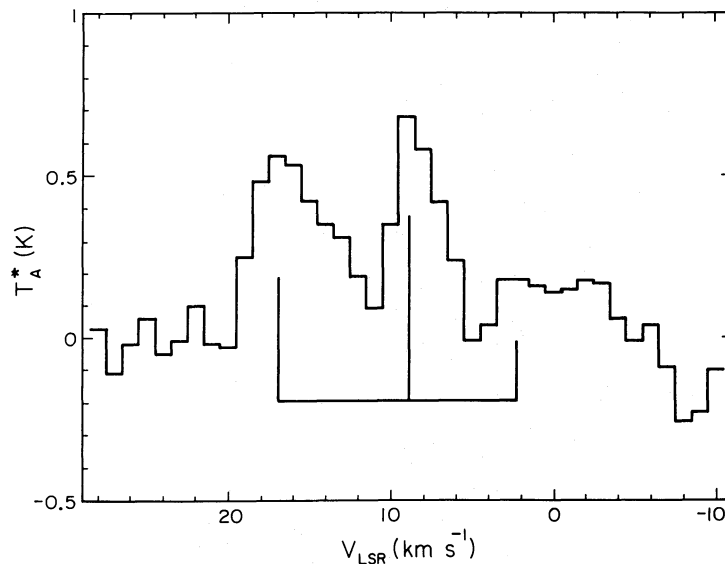


FIG. 2.—Observed HCl $J = 1 \rightarrow 0$ spectra toward OMC-1. The measurements were spaced by 1 km s^{-1} but have been Hanning smoothed to a resolution of 2 km s^{-1} . The velocity scale has been established using a main hyperfine component frequency of 625.9188 GHz (De Lucia, Helminger, and Gordy 1971). Vertical lines mark the expected hyperfine component positions assuming a V_{LSR} of 9 km s^{-1} , and their heights indicate the relative strengths expected for thermalized optically thin emission.

TABLE 1
SUMMARY OF OBSERVED AND LABORATORY HCl
 $J = 1 \rightarrow 0$ TRANSITION PARAMETERS

$F' \rightarrow F''$	ν_{rest} (MHz)	S	T_A^*	$\Delta\nu$ (km s^{-1})
$\frac{3}{2} \rightarrow \frac{3}{2}$	625901.6(0.1)	0.333	0.55	5.25
$\frac{5}{2} \rightarrow \frac{3}{2}$	625918.8(0.1)	0.500	0.70	3.5
$\frac{3}{2} \rightarrow \frac{1}{2}$	625932.0(0.1)	0.167	0.20	4.0

The peak antenna temperatures (T_A^*) of the three components, determined by fits of Gaussian components to the smoothed data, are 0.55, 0.70, and 0.20 K. Table 1 summarizes the observations presented in Figure 2 and some useful laboratory parameters. Because of the weakness of these lines, no mapping of the emission could be attempted. The line central velocity with respect to the local standard of rest (V_{LSR}) is $9 \pm 1 \text{ km s}^{-1}$, indicating that the emission originates in the warm, quiescent molecular cloud material ("spike" or "ridge" component), not the "hot core" component (Genzel *et al.* 1982) seen in many transitions of other molecules requiring high densities for excitation. The line width of the components, $\Delta\nu$, is $\sim 4\text{--}5 \text{ km s}^{-1}$ as determined by the Gaussian fits noted above.

IV. INTERPRETATION

a) Optical Depths and Abundance Calculations

The $J = 1 \rightarrow 0$ transition of HCl at 625.9 GHz is similar in many respects to the ground state $J_K = 1_0 \rightarrow 0_0$ transition of ammonia at 572.5 GHz, also detected from the Kuiper Airborne Observatory (Keene, Blake, and Phillips 1983). The frequencies and upper-state energies of these two transitions differ by less than 10%, and the dipole moments of HCl and NH_3 are quite similar, namely, 1.109 and 1.476 debye (Poynter and Pickett 1981). Excitation requirements of the two ground-state

transitions, which are severe, are therefore nearly equal. Furthermore, as both molecules are most likely formed from the neutral atomic species N and Cl via a series of ion-molecule hydrogen addition reactions followed by electron recombination or proton transfer, the two molecules should also sample similar regions of the cloud because of their chemical similarity. This view is supported by the fact that both transitions appear at a line velocity of 9 km s^{-1} . We shall therefore use information derived from mapping of the NH_3 ground-state transition to construct estimates of the HCl source size.

The main difference between the HCl and NH_3 ground-state transitions appears to be in their optical depths. The low T_A^* values of the HCl components could be caused either by optically thin emission from a small column density of molecules, or by optically thick emission from a source whose size is very small compared with the telescope beamwidth. The hyperfine component ratios of 2.4:3.0:0.9 are not as consistent with high optical depths (which would produce 1:1:1 ratios) as with the values expected for optically thin (2:3:1) or moderately optically thick emission. This contrasts sharply with the estimated peak optical depths (τ_p) of up to several hundred for the ammonia $J_K = 1_0 \rightarrow 0_0$ transition (Keene, Blake, and Phillips 1983).

A large difference in the peak optical depths is also suggested by the line widths of the two transitions. The derived line widths of $\sim 4\text{--}5 \text{ km s}^{-1}$ for the HCl components are slightly larger than, but very similar to, the line widths of known optically thin transitions in Orion sampling high-density quiescent cloud material, such as those from $^{13}\text{CH}_3\text{OH}$ and HCO_2CH_3 (Blake *et al.* 1984; Johansson *et al.* 1984). The somewhat larger line width of 7 km s^{-1} for the ammonia transition, however, is thought to be caused by a small intrinsic velocity width near 3 km s^{-1} broadened by very large peak optical depths (Keene, Blake, and Phillips 1983). For an intrinsic HCl velocity width of $2.6\text{--}3.0 \text{ km s}^{-1}$, standard curve-of-growth arguments produce peak optical depths on the order of $5\text{--}10$ (Phillips *et al.* 1979). The low T_A^* values detected for the $J = 1 \rightarrow 0$ transition argue that rotational line emission from HCl will not contribute as strongly to the bulk energy balance in molecular clouds as had been expected from previous theoretical arguments (Dalgarno *et al.* 1974), but that it may be significant for cloud cores or clumps in which the density is high.

Large differences in the peak optical depths of the two ground-state transitions will create significant differences in the effective source sizes of these lines because of their severe excitation requirements. Collisional cross sections of H_2 and HCl, kindly provided by Green (1984), indicate that radiative and collisional rates in the ground-state transition become equal for H_2 densities of a few $\times 10^7 \text{ cm}^{-3}$. Complete thermalization requires several times this density. Such high densities imply source sizes significantly smaller than our diffraction-limited $2'$ beam. Indeed, the estimated source size for the ammonia $J_K = 1_0 \rightarrow 0_0$ transition is $\gtrsim 35''$ for a single emitting clump, quite a bit larger than the value of $\sim 17''$ deduced from mapping of the 1_1 inversion transition (Barrett, Ho, and Myers 1977; Wilson, Downes, and Bieging 1979). The high optical depth of the ammonia ground-state transition in Orion is consistent with, and most likely responsible for, the increased effective emission area relative to the lower frequency inversion transitions. Such effects are not likely to be of importance for the HCl $J = 1 \rightarrow 0$ transition, however. For example, if the HCl lines are moderately optically thick, the detected antenna temperatures along with an excitation temperature of 70 K, a diffraction-

limited beam size of $2'$, and a source coupling efficiency (η_c) of $\lesssim 0.6$ imply an equivalent fully filled source size of $\vartheta_s \gtrsim 15''$.

The large uncertainties in the effective source size and line opacity make estimates of the fractional abundance of HCl, $f(\text{HCl}) = N(\text{HCl})/N(\text{H}_2)$, rather difficult. One means of addressing this difficulty is to calculate $f(\text{HCl})$ using several different methods which span the estimated range of conditions. The scatter in the answers so obtained should be a relatively good measure of the uncertainty.

i) *Optically Thin Emission*

Our observed hyperfine ratios are very close to that expected for optically thin emission from a thermalized source. While extracting optical depths from hyperfine ratios has been shown to be seriously in error in some cases, most notably HCN (Snyder and Buhl 1973; Clark, Buhl, and Snyder 1974), the observed ratios do suggest that the emission is at least not highly saturated. For optically thin emission from spatially extended sources the measured antenna temperature directly reflects the column density of the lower (or upper) rotational level. However, for sources which are small compared with the telescope beam size the quantity determined is the total number of molecules in the lower, or upper, state contained within the beam. Numerically these quantities are related by the equation

$$\frac{N_u}{g_u} = \frac{3kc\Omega_B R^3}{8\pi^2 \mu^2 \nu^2 S} \int T_A^* dv, \quad (1)$$

where N_u and g_u are the upper-state total population and degeneracy, Ω_B is the main-beam solid angle, R is the distance to the source, and μ , ν , S are the dipole moment, transition frequency, and line strength.

By inserting the values of ν , S , and $\int T_A^* dv$ from Table 1 in equation (1), we estimate that there are about $N_u/g_u \approx 3 \times 10^{48}$ molecules in the $J, F = 1, 5/2$ state for an Orion distance of 480 pc (Genzel *et al.* 1981). The translation of this single-state value into a total number of HCl molecules necessarily involves some assumptions about the rotational level population distribution.

Accurate multitransition LTE fits from millimeter-wave observations of several species requiring high excitation densities have produced rotational temperatures between 70 and 140 K for the dense, quiescent molecular cloud material in Orion (Johansson *et al.* 1984; Sutton *et al.* 1985). For simplicity we shall also assume that the observed HCl emission arises from levels in or near thermal equilibrium, and that a single rotational temperature T_{ROT} of 70–100 K is sufficient to describe the rotational level population distribution. Under such conditions we have

$$N_{\text{HCl}} = Q \frac{N_u}{g_u} \exp\left(-\frac{E_u}{kT_{\text{ROT}}}\right), \quad (2)$$

where N_{HCl} is the total number of HCl molecules contained within the beam, Q is the rotational partition function, and E_u is the energy of the observed transition upper level. Partition functions for the assumed temperature limits have been calculated from an explicit sum over the rotational levels up to $J = 5$. The derived values indicate that for $70 < T_{\text{ROT}} < 100 \text{ K}$ the total number of HCl molecules in our beam is in the range $4 \times 10^{49} < N_{\text{HCl}} < 6 \times 10^{49}$. However, subthermal populations are probable in the higher rotational levels because of the rapid increase in critical excitation densities with J . Use of

a thermal population distribution will therefore produce total populations that are likely to be slightly high.

To estimate the HCl fractional abundance, we must next determine what fraction of the cloud mass in our beam is dense enough to excite the $1 \rightarrow 0$ transition ($\sim \text{few} \times 10^7 \text{ cm}^{-3}$). To do this, we shall assume that the HCl emission arises from a single clump which is spherically symmetric, with a radial density dependence of r^{-2} . The total mass of the source is constrained by the $400 \mu\text{m}$ measurements of Keene, Hildebrand, and Whitcomb (1982), which show that there are $\sim 50 M_{\odot}$ in the central $35''$ of Orion. We find that H_2 densities sufficient to equalize the HCl collisional and radiative rates are attained only over a radius of $\sim 5 \times 10^{16} \text{ cm}$, which corresponds to a projected source diameter of $\vartheta_s \lesssim 12''\text{--}15''$. The total number of H_2 molecules within such a volume is estimated to be $N_{\text{H}_2} \lesssim (10\text{--}12) \times 10^{57}$. A lower limit to the HCl fractional abundance of $f(\text{HCl}) \gtrsim (3\text{--}6) \times 10^{-9}$ is derived from the number of H_2 and HCl molecules noted above.

A single Gaussian source distribution constrained by the $400 \mu\text{m}$ measurements produces peak central densities of approximately $3 \times 10^6 \text{ cm}^{-3}$, at least a factor of 10 below that required for thermalization. However, the Orion cloud is known to be quite inhomogeneous, and it is therefore likely that densities on the order of 10^7 cm^{-3} are present in dense clumps of gas rather than in a single region. For example, recent $2''$ resolution VLA maps of ammonia have shown that the NH_3 "spike" component arises from distinct optically thin clumps with temperatures of about 100 K spread over $\sim 10''\text{--}20''$ (Pauls *et al.* 1983). The minimum average density of these clumps is calculated to exceed 10^6 cm^{-3} , with peak densities reaching nearly 10^8 cm^{-3} . By modeling the two clumps present in the composite VLA ammonia map as spherical Gaussian sources with a FWHM of $4''$ and central densities of 10^8 cm^{-3} , we find that approximately $5 \times 10^{57} \text{ H}_2$ molecules are contained within these clumps at densities sufficient to excite the HCl ground-state transition. This produces an HCl fractional abundance of approximately 10^{-8} , about a factor of 2 above the r^{-2} single-source estimate.

ii) Moderate Optical Depth Emission

The small source size derived above for thermalized emission indicates that it is highly unlikely that the ground-state emission is optically thin. Indeed, this size of $\vartheta_s \lesssim 12''\text{--}15''$ agrees well with the optically thick source size derived earlier and with the estimated $\text{NH}_3(1, 1)$ inversion transition ($\tau_p \sim 1\text{--}2$) source size of $\sim 17''$. Combined with the line-width arguments discussed earlier, the small source size suggest that the HCl emission is in fact moderately optically thick, with peak optical depths on the order of 5–10. Significantly higher optical depths are unlikely, since the line width, effective source size, and T_A^* would be substantially larger, closer to the values observed for NH_3 .

For sources in which microturbulence is the dominant intrinsic line-broadening mechanism, standard arguments show that

$$\tau_p = \left(\frac{4 \ln 2}{\pi} \right)^{1/2} \frac{c^2 A_{ul} N_u}{8\pi\nu^2 \Delta\nu g_u} \left[\exp\left(\frac{h\nu}{kT_{\text{ROT}}} \right) - 1 \right], \quad (3)$$

where N_u is the upper-state column density (molecules cm^{-2}), A_{ul} is the Einstein spontaneous emission coefficient (s^{-1}), and $\Delta\nu$ is the line FWHM (Hz). If we assume that τ_p lies between 5 and 10 and also that a single rotational temperature T_{ROT} between 70 and 100 K describes the rotational level population

distribution, then equation (3) yields total column densities between $N_{\text{HCl}} \approx (0.5\text{--}2.0) \times 10^{16} \text{ HCl cm}^{-2}$. Subthermal population of the higher J states could cause this estimate to be somewhat high, but the higher assumed optical depths will reduce it somewhat by lowering the critical excitation density via photon trapping.

To convert the derived HCl column density into a fractional abundance, we need to know the H_2 column density. Liszt *et al.* (1974) and Westbrook *et al.* (1976), among others, have deduced values of $\sim (3\text{--}7) \times 10^{23} \text{ H}_2 \text{ cm}^{-2}$ for the Orion "spike," or "ridge" component. We estimate an average H_2 column density of $\sim 10^{24} \text{ H}_2 \text{ cm}^{-2}$ from the spherically symmetric r^{-2} source model described above by assuming an effective source diameter of $15''$, a value similar to that obtained for the high-density "torus" material surrounding IRc 2 (Plambeck *et al.* 1982). Adopting the nominal value of 5×10^{23} from Liszt *et al.* (1974), we see that $f(\text{HCl}) \sim (1\text{--}5) \times 10^{-8}$, about a factor of 10 higher than the lower bound derived by the optically thin calculations. These estimates are approximately a factor of 2–10 below the HCl upper limit of $\sim 10^{-7}$, which assumes a depletion factor of 3 for Cl (Jura and York 1978) and assumes that all gas-phase chlorine exists as HCl. Observation of the $\text{H}^{37}\text{Cl } J = 1 \rightarrow 0$ transition at 625.0 GHz would greatly reduce the ambiguity of these limits by producing much more direct and accurate estimates of the transition opacities, provided that a solar $^{35}\text{Cl}/^{37}\text{Cl}$ ratio can be assumed.

iii) Optically Thick, Subthermal Emission

As noted above, the extremely high densities required for the equilibration of collisional and radiative rates in HCl are likely to induce subthermal populations of rotational levels above the ground state, rendering thermal calculations of the total column density inaccurate. However, for clouds with large velocity gradients, lines which are optically thick and strongly subthermal may be treated using the escape probability approximation (Watson 1984). In the optically thick and subthermal limit, the number of photons leaving the cloud is proportional to the number of collisional excitations, just as for optically thin lines. This arises because collisional de-excitations occur so infrequently that only a small fraction of the photons is destroyed before leaving the cloud, even though these photons are absorbed and reemitted several times. Formally, the absorption and reemission processes are handled by multiplying the Einstein A -coefficients by the photon escape probabilities, which causes the calculation to be geometry-dependent. For a spherically symmetric cloud, one may show that the Rayleigh-Jeans brightness temperature T_B and the molecular column density N_{mol} are related by

$$T_B = \frac{hc^2}{8\pi k\nu} \sum_i \gamma_{0i} n_{\text{H}_2} N_{\text{mol}} \Omega_B, \quad (4)$$

where γ_{0i} is the collisional rate from the ground state to the i th rotational level ($\text{cm}^3 \text{ s}^{-1}$) and n_{H_2} is the molecular hydrogen density (molecules cm^{-3}) (Watson 1984). Once again, the collisional rate coefficients have been provided by Green (1984). To calculate T_B from our measured T_A^* , we have assumed a source size of $15''$ in conjunction with our $2'$ diffraction-limited beam and a source coupling efficiency of $\eta_c \lesssim 0.6$.

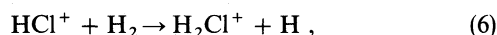
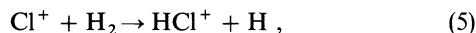
The major source of uncertainty in equation (4) is the H_2 density assumed for the emitting region. Several studies of high dipole moment molecules like CH_3CN and H_2CO have shown that the mean Orion core density is as high as 10^6 cm^{-3} (Loren and Mundy 1984; Wootten, Loren, and Bally 1984), although

earlier CO and CS surveys by Liszt *et al.* (1974) and Goldsmith *et al.* (1980) conclude only that $n_{\text{H}_2} \gtrsim 2 \times 10^5 \text{ cm}^{-3}$. In order to set an upper limit to the HCl column density, we shall assume that $n_{\text{H}_2} \gtrsim 5 \times 10^5$. Inserting these values in equation (4) yields $N_{\text{HCl}} \lesssim 5 \times 10^{15} \text{ cm}^{-2}$, from which we conclude that $f(\text{HCl}) \lesssim 1 \times 10^{-8}$. Peak optical depths in excess of 10 are produced by such values, which indicate that the ratio of the upper and lower state populations is about $n_1/n_0 \sim \tau n_{\text{H}_2} \gamma_{10}/A_{10} \sim 0.1$ —quite a bit less than the thermalized value of $(n_1/n_0)_{\text{therm}} \sim 2$. This estimate, which is independent of the assumed density, shows that the higher J levels appear to be subthermal. The estimated fractional abundance therefore lies between the limits derived in the thermalized optically thin and optically thick calculations, even though the opacity is fairly high.

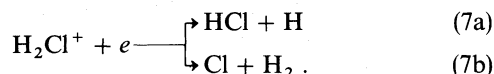
Not surprisingly, these three methods show a considerable amount of scatter because our information is incomplete. They can be summarized as showing that the abundance of HCl relative to H_2 in the gas phase lies in the range $(0.5\text{--}5.0) \times 10^{-8}$ for dense interstellar clouds. Optical studies of diffuse clouds with the *International Ultraviolet Explorer (IUE)* have shown that the abundance of HCl is at least 10 times less than the quantitative model predictions of Black and Dalgarno (1977) (Smith *et al.* 1980 and references therein). Thus, the amounts of hydrogen chloride present in both diffuse and dense molecular clouds appear to be below those predicted by earlier theoretical models of interstellar chlorine chemistry in these objects.

b) Chlorine Chemistry

Recent theoretical and experimental work on various aspects of this chemistry has resolved most of the discrepancies for HCl in diffuse clouds. In these objects HCl is thought to be built up from ionized atomic chlorine by the following set of reactions:

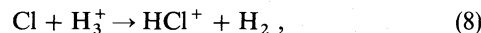


followed by electron recombination:



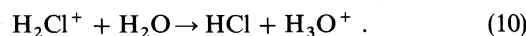
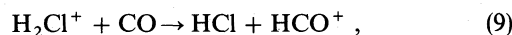
The major destruction process for HCl is photodissociation by the visible and UV photons permeating the cloud. Extensive theoretical calculations by van Dishoeck, van Hemert, and Dalgarno (1982) have shown that previous estimates of the dissociation rates, which included only transitions to the $A^1\Pi$ state, were low by as much as a factor of 3–4. Both reactions (5) and (6) are rapid at room temperature, but reaction (5) may well possess a modest energy barrier because of its small exothermicity ($\sim 5 \text{ kcal mole}^{-1}$). Furthermore, although experimental measurements by Smith and Adams (1981) have shown that both reactions are rapid and fairly temperature-insensitive (there is some disagreement, however, over reaction (5); see Cates, Bowers, and Huntress 1981), they also suggest that the branching ratio for channel (7a) could be 10% or lower. Inclusion of the modified dissociation rates and ion-molecule rate constants in the detailed reaction networks reduces the predicted HCl abundance to well below the observed upper limits in diffuse clouds if a slow temperature-dependent rate equation is used for reaction (5), and raises the Cl^+ estimates to near that observed (van Dishoeck 1984).

The predictions are less certain for dense clouds, in which the formation of hydrogen chloride is thought to be initiated not by Cl^+ but by neutral atomic chlorine:



followed by reactions (6) and (7). No experimental rates are available for reaction (8). The reaction sequence initiated by reaction (8) and terminated by H_2Cl^+ is capable of converting most or all of the gas-phase Cl into hydrogen chloride within cloud lifetimes in the absence of competitive processes. As pointed out by Dalgarno *et al.* (1974), HCl is fairly unreactive toward abundant neutral species like O and OH, but reactions with positive ions are only now being studied in the laboratory and are likely to be the most important gas-phase loss processes. Recent work by Blake, Anicich, and Huntress (1985) has identified the major reaction routes of HCl with several of the more abundant interstellar ions. We briefly outline below the results of their theoretical reanalysis of interstellar chlorine chemistry.

The proton affinity of HCl is rather low, slightly below that of CO. Thus, H_2Cl^+ reacts rapidly via proton transfer with abundant interstellar neutral molecules such as CO or H_2O :



For the very low electron abundance predicted by large-scale models of dense, quiescent interstellar clouds (Prasad and Huntress 1980; Leung, Herbst, and Huebner 1984), reactions (9) and (10) proceed at significantly faster rates than the electron recombination processes listed in formulas (7a) and (7b). Only when the fractional electron abundance exceeds 10^{-6} , which is above the inferred upper limits in dense clouds from observations of CO and HCO^+ (Wooten, Loren, and Snell 1982), do channels (7a) and (7b) compete effectively with proton transfer to CO. Thus the major impediments to HCl production in diffuse clouds do not affect the HCl abundance in dense molecular clouds. One might therefore expect that the entire gas-phase chlorine population would be present as HCl. However, H_2Cl^+ and HCl react rapidly with C and C^+ to produce CCl^+ , which is isoelectronic with CS and quite stable. Except for charge transfer and recombination reactions with electrons, the CCl^+ ion reacts rapidly only with atomic oxygen and the molecular species NH_3 and H_2CO , the net effect of which is to regenerate Cl. A circulatory pattern is therefore established in which all species except Cl and HCl have only trace abundances. The relative abundance ratio of Cl and HCl is fairly insensitive to order-of-magnitude variations in the chemical composition of the model molecular cloud, with HCl occupying between 25% and 65% of the gas-phase chlorine abundance. Thus, for a depletion factor of 3 the new model predicts a gas-phase HCl fractional abundance of $(2.5\text{--}6.0) \times 10^{-8}$, in good agreement with the calculations for the optically thick case described earlier.

If we combine the results of the theoretical model of chlorine chemistry with our observations, limits on the Cl depletion in dense interstellar clouds may be obtained. We find that the chlorine depletion in dense clouds lies in the range 3–30. The diffuse cloud survey of Jura and York (1978) found that chlorine is depleted by no more than a factor of 3, but Harris, Gry, and Bromage (1984) have recently suggested that the chlorine depletion in diffuse clouds varies strongly with density and that chlorine may in fact be depleted by a factor of 5 or more. If

true, these results imply that the chlorine depletion may level off at high densities and that chlorine remains fairly volatile even in dense molecular clouds, unlike other more refractory elements, such as Si and P, which appear to be depleted by factors approaching 100 in such objects.

To summarize, relatively weak emission from the $J = 1 \rightarrow 0$ transition of HCl has been detected at 625.9 GHz from OMC-1. The implied upper limit to the HCl fractional abundance is below previous theoretical estimates for this molecule, reducing the expected contribution of the $J = 1 \rightarrow 0$ transition to the thermal balance of molecular clouds. A reanalysis of the chlorine chemistry suggests that Cl and HCl are the dominant

components of the gas-phase chlorine abundance, and that chlorine is depleted by at most a factor of 30 in dense interstellar clouds.

We would like to thank the crew of the Kuiper Airborne Observatory for their effective support of these observations; V. G. Anicich and W. T. Huntress, Jr., for helpful discussions about the chemistry of interstellar chlorine; and S. Green for providing the collisional excitation coefficients. This research has been supported by NASA grant NAG 2-1 to the California Institute of Technology.

REFERENCES

- Barrett, A. H., Ho, P. T. P., and Myers, P. C. 1977, *Ap. J. (Letters)*, **211**, L39.
 Black, J. H., and Dalgarno, A. 1977, *Ap. J. Suppl.*, **34**, 405.
 Blake, G. A., Anicich, V. G., and Huntress, W. T., Jr. 1985, *Ap. J.*, submitted.
 Blake, G. A., Sutton, E. C., Masson, C. R., Phillips, T. G., Herbst, E., Plummer, G. M., and De Lucia, F. C. 1984, *Ap. J.*, **286**, 586.
 Cates, R. D., Bowers, M. T., and Huntress, W. T., Jr. 1981, *J. Phys. Chem.*, **85**, 313.
 Clark, F. O., Buhl, D., and Snyder, L. E. 1974, *Ap. J.*, **190**, 539.
 Dalgarno, A., de Jong, T., Oppenheimer, M., and Black, J. H. 1974, *Ap. J. (Letters)*, **192**, L37.
 De Lucia, F. C., Helminger, P., and Gordy, W. 1971, *Phys. Rev. A*, **3**, 1849.
 Genzel, R., Downes, D., Ho, P. T. P., and Bieging, J. 1982, *Ap. J. (Letters)*, **259**, L103.
 Genzel, R., Reid, M. J., Moran, J. M., and Downes, D. 1981, *Ap. J.*, **244**, 884.
 Goldsmith, P. F., Langer, W. D., Schloerb, F. P., and Scoville, N. Z. 1980, *Ap. J.*, **240**, 524.
 Green, S. 1984, private communication.
 Harris, A. W., Gry, G., and Bromage, G. E. 1984, *Ap. J.*, **284**, 157.
 Johansson, L. E. B., Andersson, C., Ell der, J., Friberg, P., Hjalmarson, B., Irvine, W. M., Olofsson, H., and Rydbeck, G. 1984, *Astr. Ap.*, **130**, 227.
 Jura, M. 1974, *Ap. J. (Letters)*, **190**, L33.
 Jura, M., and York, D. G. 1978, *Ap. J.*, **219**, 861.
 Keene, J., Blake, G. A., and Phillips, T. G. 1983, *Ap. J. (Letters)*, **271**, L27.
 Keene, J., Hildebrand, R. H., and Whitcomb, S. E. 1982, *Ap. J. (Letters)*, **252**, L11.
 Leung, C. M., Herbst, E., and Huebner, W. F. 1984, *Ap. J. Suppl.*, **56**, 231.
 Linsky, J. L. 1973, *Ap. J. Suppl.*, **25**, 163.
 Liszt, H. S., Wilson, R. W., Penzias, A. A., Jefferts, K. B., Wannier, P. G., and Solomon, P. M. 1974, *Ap. J.*, **190**, 557.
 Loren, R. B., and Mundy, L. G. 1984, *Ap. J.*, **286**, 232.
 Pauls, T. A., Wilson, T. L., Bieging, J. H., and Martin, R. N. 1983, *Astr. Ap.*, **124**, 23.
 Phillips, T. G., Huggins, P. J., Wannier, P. G., and Scoville, N. Z. 1979, *Ap. J.*, **231**, 720.
 Phillips, T. G., and Jefferts, K. B. 1974, *IEEE Trans. Microwave Theory Tech.*, **22**, 1290.
 Plambeck, R. L., Wright, M. C. H., Welch, W. J., Bieging, J. H., Baud, B., Ho, P. T. P., and Vogel, S. N. 1982, *Ap. J.*, **259**, 617.
 Poynter, R. L., and Pickett, H. M. 1981, *Submillimeter, Millimeter, and Microwave Spectral Line Catalogue* (JPL Pub. 80-23, Rev. 1).
 Prasad, S. S., and Huntress, W. T., Jr., 1980, *Ap. J. Suppl.*, **43**, 1.
 Smith, D., and Adams, N. G. 1981, *M.N.R.A.S.*, **197**, 377.
 Smith, P. L., Yoshino, K., Black, J. H., and Parkinson, W. H. 1980, *Ap. J.*, **238**, 874.
 Snyder, L. E., and Buhl, D. 1973, *Ap. J. (Letters)*, **185**, L79.
 Sutton, E. C., Blake, G. A., Masson, C. R., and Phillips, T. G. 1985, *Ap. J. Suppl.*, in press.
 van Dishoeck, E. F. 1984, Ph.D. thesis, University of Leiden.
 van Dishoeck, E. F., van Hemert, M. C., and Dalgarno, A. 1982, *J. Chem. Phys.*, **77**, 3693.
 Watson, D. M. 1984, *Galactic and Extragalactic Infrared Spectroscopy*, ed. M. F. Kessler and J. P. Phillips (Dordrecht: Reidel), pp. 195-219.
 Westbrook, W. E., Werner, M. W., Elias, J. H., Gezari, P. Y., Hauser, M. G., Lo, K. Y., and Neugebauer, G. 1976, *Ap. J.*, **209**, 94.
 Wilson, T. L., Downes, D., and Bieging, J. 1979, *Astr. Ap.*, **71**, 275.
 Wootten, A., Loren, R. P., and Bally, J. 1984, *Ap. J.*, **277**, 189.
 Wootten, A., Loren, R. P., and Snell, R. L. 1982, *Ap. J.*, **255**, 160.
 Wright, E. L., and Morton, D. C. 1979, *Ap. J.*, **227**, 483.

GEOFFREY A. BLAKE, JOCELYN KEENE, and T. G. PHILLIPS: California Institute of Technology, 320-47 Pasadena, CA 91125