

THEORETICAL STUDIES OF DIFFUSE CLOUD CHEMISTRY

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ABSTRACT. Some recent work on diffuse cloud chemistry is summarized. Distinctions between gas phase chemistry in steady state and alternative mechanisms are discussed.

1. INTRODUCTION

Theoretical descriptions of diffuse interstellar clouds are needed to complement observations in order to infer the nature of the clouds and the role they play in the general evolution of the Galaxy. In principle, theories of diffuse cloud chemistry provide the framework through which spectroscopic measurements can be used as diagnostic probes of temperature, density, intensity of background starlight, and local cosmic ray flux. In practice, uncertainties about basic processes often limit the accuracy with which these properties can be derived from observation to factors of two. In a more qualitative--but fundamental--sense, it is not yet fully established (1) whether diffuse clouds represent a single class of interstellar structure, (2) whether abundances in diffuse clouds reflect a chemical steady state or whether many observed column densities are controlled by impulsive or time-dependent effects, (3) whether the grains play a mostly passive or active role in the chemistry of species other than H_2 , and (4) how diffuse clouds are related in a dynamical and evolutionary sense to thick, dense molecular clouds. Even if we respond affirmatively to Dalgarno's (1986) question "Is interstellar chemistry useful?", we must recognize that our knowledge must be improved, both in matters of detail (e.g. determining densities and temperatures in specific clouds) and in conceptual matters (e.g. establishing whether steady-state gas-phase chemistry can adequately describe the composition of any cloud).

In a brief review, only a few topics can be addressed and reference to the literature is necessarily highly selective. Recent reviews of diffuse cloud chemistry include those of Dalgarno (1986) and Crutcher and Watson (1985). The following remarks draw heavily upon recent comprehensive models of diffuse clouds (van Dishoeck and Black 1986), which are based on the point of view that it is important to try to

account for all of the observable properties of the best studied individual clouds. Less specific models of general diffuse clouds have been discussed recently by Viala (1986) and Mann and Williams (1985).

2. GAS-PHASE CHEMISTRY IN STEADY STATE

For purposes of discussion, we assume that H_2 forms on grain surfaces and is destroyed by ultraviolet starlight through fluorescent photodissociation initiated by line absorption. The abundance and excitation of H_2 are consequently strongly depth-dependent, and the internal structure of a diffuse cloud is governed by the transfer of dissociating radiation (Jura 1975; Black and Dalgarno 1977; Federman, Glassgold, and Kwan 1978; van Dishoeck and Black 1986). Carbon chemistry is thought to begin with a radiative association process



and to lead directly to CH and CH_2 through subsequent ion-molecule reactions and ion-electron recombination. Reactions of C^+ with CH and CH_2 lead to C_2 and C_2H . Ionization of H and H_2 by cosmic rays produces H^+ and H_3^+ and the latter usually reacts with H_2 to form H_3^+ . Oxygen chemistry results from



and



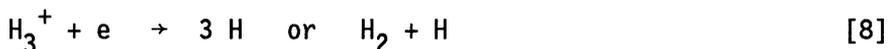
followed by various reactions that ultimately form OH and H_2O . The ubiquitous CO molecule can arise from reactions of C and C^+ with oxygen-bearing species or from reactions of small hydrocarbons with oxygen. Deuterium-bearing molecules form at different rates than their hydrogen-bearing counterparts largely because of the importance of reactions like



It is uncertain whether the formation of nitrogen-bearing molecules can be generated effectively by a somewhat unusual reaction



(Huntress 1977), the alternative being neutral-neutral reactions of CH and C_2 with N to form molecules like CN (e.g. Federman, Danks, and Lambert 1984). A significant development is the recent recognition that



is unusually slow for ground-state ions at low temperature (Michels and Hobbs 1984, Smith and Adams 1984). The rate coefficient, k_8 , is not well determined at present. In diffuse clouds where H_3^+ arises from cosmic ray ionizations at a rate ζ_0 s⁻¹ and is removed by [3] and [8], its density is approximately

$$n(H_3^+)/n(H_2) = 2 \times 10^{-6} (\zeta_0/5 \times 10^{-17}) (300/n) / [8\delta_O + F]$$

where $n = n(H) + 2n(H_2)$ is the total density, $F = 5\delta_C (k_8/10^{-9})$, and δ_O and δ_C are the factors by which the abundances of oxygen and carbon are depleted with respect to their solar values. In a diffuse cloud, where the column density, $N(H_2) > 4 \times 10^{20}$ cm⁻², and $\delta_O = \delta_C = 0.5$, the column density of H_3^+ may be large enough, $N(H_3^+) > 2 \times 10^{14}$ cm⁻², to be detectable by infrared absorption line techniques (Oka 1981). Indeed, it might be possible to use such observations to place limits upon the value of k_8 , provided that the cosmic ray flux, density, and abundances of O and C+ can be estimated for the same cloud. Although large photodissociation rates for H_3^+ have propagated through the literature (e.g. Black and Dalgarno 1977), they cannot be justified.

The previously unexpected large abundance of H_3^+ in diffuse clouds will have many other consequences for the chemistry. For example, if reaction [7] is relatively efficient, then the predicted abundances of NH may approach existing upper limits in some clouds (van Dishoeck and Black 1986, Viala 1986). Reactions of nitrogen hydrides with carbon will then provide the dominant source of CN in clouds of low density, and NH_2 may be present in detectable amounts in clouds where $N(H_2) > 10^{21}$ cm⁻².

In general, concentrations of the most abundant neutral species are limited by photodissociation in diffuse clouds, which are translucent to ultraviolet starlight. Understanding of crucial photodissociation processes has been improving in recent years (see van Dishoeck 1987). In particular, processes affecting the abundance of OH have been studied extensively, so that the column densities of OH and HD can still be considered useful probes of the cosmic ray ionization rate (Black and Dalgarno 1973, O'Donnell and Watson 1974).

The steady state models of van Dishoeck and Black (1986) have continuous gradients in density and temperature that satisfy hydrostatic equilibrium for pressure-bounded sheets; describe the abundance and excitation of a 470 level hydrogen molecule as functions of depth; incorporate a gas-phase chemistry for 120 species made of H, C, N, O, their principal isotopes, and Cl; and treat the excitation of C₂, CO, C, C+, and O. The available observations of the clouds toward ζ Oph, ζ Per, \circ Per, and χ Oph were analyzed in detail. If the rate of [8] is low, the OH abundances suggest $\zeta_0 \approx 7 \times 10^{-17}$ s⁻¹, and the HD abundances are in harmony with an overall deuterium abundance $[D]/[H] = (1.5 \pm 0.5) \times 10^{-5}$. For the ζ Per cloud, the excitation of H₂, C₂, and the atomic fine-structure levels are all consistent with a central density $n = 250$ -500 cm⁻³ and temperature $T \approx 30$ K. In the case of the principal cloud toward ζ Oph, the central temperature is $T \approx 25$ K. The central density, $n = 350$ -800 cm⁻³, inferred from the abundance and excitation of H₂ in steady state is somewhat higher than that suggested by the other

diagnostics, but in any event the density must be lower than the value previously suggested by Black and Dalgarno (1977). The lack of agreement among density diagnostics for ζ Oph can be resolved if part of the excited H_2 in $J=2,3$, and 4 is contributed by a thin layer of shock-heated gas (cf. Draine 1986).

In this brief summary of conventional gas phase chemistry, we have mentioned three specific, crucial reactions, [1], [7], and [8], whose rates are poorly known. At present these rates must enter as disposable parameters in the comparison of chemical models with observation. Even some of the processes affecting the abundance and excitation of H_2 are imperfectly understood. The literature contains radically different predictions about the internal energy distributions of newly-formed hydrogen molecules (Hollenbach and Salpeter 1970; Hunter and Watson 1978; Allen and Robinson 1976; Leonas and Pjarnpuu 1981; and Duley and Williams 1986). Moreover, the total H_2 formation efficiency is not accurately known. It is perhaps not surprising, therefore, that elaborate model analyses of the best observed diffuse clouds are still unable to establish values of physical parameters like density to an accuracy much better than a factor of two in those clouds (van Dishoeck and Black 1986). On the other hand, within these uncertainties it appears possible to infer densities, cosmic ray fluxes and intensities of ultraviolet starlight using theoretical cloud models. Perhaps more importantly at this stage, the model analyses are helpful in identifying crucial processes that require further study.

3. ALTERNATIVE CHEMISTRIES AND DEPARTURES FROM STEADY STATE

Failures or inadequacies of conventional chemical models can be taken to indicate either that certain details such as individual rate coefficients are incorrect or that basic premises are faulty. It is usually assumed that abundances in diffuse clouds are in steady state because the abundances of the most important species are controlled by photodissociation or by rapid reactions for which the time scales are typically short, 10^4 y or less. One striking exception is H_2 : owing to the effective self-shielding of this molecule, its lifetime (and the corresponding formation time) can vary from 10^3 y at the boundary to 5×10^6 y or more at the center of diffuse clouds of modest thickness, $A_V \approx 1$. Tarafdar et al. (1985) have recently considered the chemical and dynamical evolution of diffuse clouds and have concluded that even low mass clouds initially of low density can collapse to achieve $n=10^6 \text{ cm}^{-3}$ on time scales of the order of 3×10^6 y. Of course such collapse can shorten the approach to chemical steady state (see also Gerola and Glassgold 1978), but such short cloud lifetimes would suggest that very few diffuse clouds currently at $n=100\text{-}500 \text{ cm}^{-3}$ will exhibit H_2/H abundance ratios in steady state throughout. This situation will be less desperate if other agents (e.g. magnetic fields) act to retard the collapse of diffuse structures. Previous investigations of time-dependent H and H_2 abundances in dense clouds have not included effects of ultraviolet photodissociation and depth-dependent structure (Allen and Robinson 1976, Iglesias 1977) and general treatments of time-

dependent interstellar chemistry (e.g. Graedel, Langer, and Frerking 1982; Watt 1983; Leung et al. 1984) fix the relative abundances of H and H₂ and ignore their histories.

Another form of non-equilibrium chemistry is that expected to occur in shock-heated gas. This subject is addressed in detail elsewhere in this volume. It has been suggested that weak shocks in diffuse clouds provide the site of formation of the anomalously abundant CH⁺ ion (Elitzur and Watson 1978, 1980); if so, the shocked regions must necessarily contribute substantially to the column densities of other species such as OH, CH, CO, and rotationally-excited H₂ (Mitchell and Deveau 1983; Mitchell and Watt 1985; Draine and Katz 1986a,b; Draine 1986; Flower, Pineau des Forets, and Hartquist 1985; Pineau des Forets et al. 1985; Graff and Dalgarno 1986). Some predictions are sensitive to whether the shocks are non-magnetic or multiple-fluid, magnetohydrodynamic ones, and care must be taken in accounting for non-equilibrium effects on reaction rates (Graff and Dalgarno 1986; Herbst and Knudson 1981). Weak, non-dissociating shocks are probably unable to produce detectable amounts of vibrationally-excited H₂, whereas ultraviolet absorption and fluorescence in steady state naturally yield H₂ in v>1 characterized by excitation temperatures exceeding 6000 K. Table I lists examples of predicted equivalent widths of Lyman system lines arising in v">0 for two particular steady-state models of the diffuse clouds toward ζ Per and ζ Oph (van Dishoeck and Black 1986). Although the uncertainties in dust properties, collision rates, and densities allow for factor-of-two variations in the predicted values, failure to detect these lines at approximately the predicted level would

TABLE I. Equivalent Widths of H₂ B-X Lines in Steady-State Clouds

v'	v"	Line	λ (Å)	W _λ (mÅ):	ζ Per [Model F]	ζ Oph [Model E]
0	1	R(1)	1162.171		0.6	1.3
0	2	R(1)	1217.645		1.0	2.1
0	3	R(1)	1274.922		1.3	2.7
0	3	R(2)	1276.325		1.0	2.2
0	4	R(1)	1333.797		1.2	2.6
0	4	R(2)	1335.131		1.0	2.1
0	5	R(1)	1393.963		0.9	1.8
0	6	R(1)	1454.972		0.5	1.0
1	6	R(1)	1427.707		0.4	0.9

be a fairly clear indication that shock-heated gas is responsible for a large fraction of the observed rotationally-excited H₂. In clouds where even higher ultraviolet fluxes have been suggested (Frisch and Jura 1980; White 1984) lines of H₂(v>0) may be even more prominent.

Although the presence of ions and high rates of photodissociation in diffuse clouds suggest that gas phase chemistry dominates, the alternative view that some species other than H₂ form on grain surfaces

must also be considered (Mann and Williams 1984; Tielens and Hagen 1982; Tielens 1983; Leitch-Devlin and Williams 1985). Some tests are possible. The small upper limit on the NH/OH abundance ratio in several diffuse clouds has been used (Crutcher and Watson 1976) to argue that these species do not form on grain surfaces with comparable efficiencies.

Intermediate between small molecules and solid dust particles are the large polycyclic aromatic hydrocarbon molecules that have recently been suggested as carriers of the diffuse interstellar bands (van der Zwet and Allamandola 1985; Leger and d'Hendecourt 1985; Crawford et al. 1985). In order for such large molecules to exist in appreciable amounts in diffuse clouds they must be very unlikely to dissociate upon absorption of ultraviolet radiation and thus must be very adept at internal conversion of absorbed energy (cf. Douglas 1977). Further studies of photodissociation processes in large molecules are needed.

4. DISCUSSION

A few details of diffuse cloud chemistry have been discussed and suggestions have been made about assessing the range of applicability of gas phase photochemistry in steady state. Ultimately one wants to understand what part the diffuse clouds play in the evolution of the interstellar medium. In this connection it will be important to give more attention to clouds with visual extinctions $A_V=1.5-5$ mag that are thicker than the best-studied diffuse clouds. Before the body of optical absorption line data on thicker clouds (Hobbs, Black and van Dishoeck 1983; Lutz and Crutcher 1983; van Dishoeck and de Zeeuw 1984; Crutcher 1985; Crutcher and Chu 1985; Cardelli and Wallerstein 1985; van Dishoeck and Black, in preparation) grows further, there is time for theorists to predict how the column densities of observable molecules should increase with increasing total column density and whether additional species should be detectable. This would help to bridge the conceptual barrier between diffuse clouds and dark, dense clouds, and might also help to legitimize the enterprise of interstellar chemistry should any such predictions be verified.

The chemistry of the CO molecule, in particular, needs to be much better understood. In thin diffuse clouds, CO accounts for a small fraction of the gas phase carbon, but it is widely believed to contain most of the carbon in clouds only a few times thicker. The depth-dependence of the abundance of and isotope fractionation in CO is a complicated problem (Glassgold and Langer 1976; Bally and Langer 1982; Chu and Watson 1983; Glassgold et al. 1985; Tielens and Hollenbach 1985a,b; van Dishoeck and Black, in preparation) that demands more work, but progress will depend partly on improvements in basic spectroscopic data.

Preparation of this review was aided greatly by discussions with E. F. van Dishoeck and was supported in part by NASA through Theoretical Astrophysics grant NAGW-763 to the University of Arizona.

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DISCUSSION

GLASSGOLD: Would you comment in more detail how the photo rates were determined, in particular how the radiation field was determined and the possible effects of the illuminating stars?

BLACK: We adopt the wavelength dependence of Draine (1978) for background UV starlight and use a scaling factor I_{UV} as a disposable parameter. Depth dependences of continuous absorption processes are computed using an adaptation of the methods of Roberge, Dalgarno and Flaunery (1980). Line absorption processes (e.g. self-shielding of H_2 and CO) are treated in detail in a manner consistent with the results of Federman, Glassgold and Kwan. The interpretation of C_2 excitation suggests a uniform intensity in the far red while the excitation and abundance of H_2 indicate $I_{UV} \approx 2 - 5$ with factors of two differences from cloud to cloud.

WILLIAMS: I will describe later in my talk a mechanism for H_2 formation on surfaces in which the v, J state is well specified.

Would you not agree that the modelling process cannot give unique results? In particular, OH may not be a good indicator of the cosmic ray ionization rate especially if surface reactions contribute to OH formation. Quite consistent models including molecular formation on grains have been described recently by Mann and Williams (MNRAS 1984, 1985).

BLACK: The papers of Mann and Williams are, of course, cited. The current results for four clouds are consistent with the same values of cosmic ray ionisation rate and deuterium abundance in matching the observed OH and HD column densities that are sensitive to cosmic ray rates in gas phase theories. I agree that surface processes may still be important for some species. It is our intention to use comprehensive models like those described to put limits on the surface contributions and to suggest observational tests. Although the models are not currently unique, some parts of parameter space can be uniquely excluded.

LANGER: If the observed clouds are really the envelopes of larger cloud structures, would this change the modelling and interpretation of the cloud properties?

BLACK: The morphology of a diffuse cloud is generally quite poorly defined. Comparison of models computed with isotropic and anisotropic radiation fields, for example, suggests that the effects you mention will be not larger than the uncertainties in computed results that arise from our current lack of understanding of some crucial microscopic processes.

SHAPIRO: Since synthesis of molecules in clouds can be effected by cosmic rays and/or by shocks, how can we tell which of these has been the dominant process in a given context?

BLACK: Cosmic rays are generally considered to be responsible for production of observed (HCO^+ , NH_2^+ , ...) and inferred (e.g. H_3^+) ions in thick molecular clouds. Although many ions can also be produced by starlight photo-ionisation in diffuse clouds, the production of HD and OH are largely due to cosmic ray ionisation that yield H^+ and H_3^+ . In the absence of definitive observational signatures of shocks in diffuse clouds, the evidence for them is indirect and often subtle. A major thrust of this review was to explore the limits of current steady state theory and to use steady state models to suggest a fairly conclusive observational diagnostic, *viz.*, vibrationally excited H_2 that cannot be produced by weak shocks.