

MOLECULE FORMATION IN COOL, DENSE INTERSTELLAR CLOUDS

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ABSTRACT

A discussion is given of the general processes and considerations that arise in attempting to understand molecular reactions in cool, dense interstellar clouds. Basic elements of the gas phase, "ion-molecule" scheme are given explicitly before surveying topics in which there is considerable current activity. These topics include: (i) refined comparisons of prediction and observation for species of "intermediate" complexity, (ii) numerical computations of cloud models which include numerous chemical reactions and molecular species, (iii) formation of the complex molecules, (iv) isotope fractionation in interstellar molecules and (v) possible contributions from chemistry in shocks.

I. INTRODUCTION

I will discuss reaction processes for molecules under physical conditions which are thought likely to be a satisfactory first approximation in much of the gas of most "dense" interstellar clouds. By dense clouds, I just mean those with extinctions $A_V \gtrsim 10$ for which the number density of the gas is $n \gtrsim 10^4 \text{ cm}^{-3}$ and the kinetic temperature T is less than about 50 K. Clearly this is not a homogeneous group of clouds. However, it seems most efficient for discussion of the chemistry to consider the impact of their differences as refinements or particular cases within a general outline.

The chief approximation for "dense clouds" is that the intensity of ultraviolet radiation is sufficiently low, as suggested by the large extinction, that photoionization and photodissociation can be ignored. In contrast, these processes have a major if not dominant effect in the chemistry of the classical "diffuse" clouds which will be discussed subsequently by A. Dalgarno. As a result, the gas in dense clouds is mainly in molecular form so that reactions which rearrange molecules are much more important than in diffuse clouds where the gas is

primarily in atomic form. Hence, the chemical reaction mechanisms tend to be qualitatively different. A further difference in approach is due to the generally poor knowledge of physical conditions in dense clouds and to the substantial uncertainties in many cases in relating the observed line intensities to molecular abundances in dense clouds. Tests of proposed reaction schemes that are insensitive to detailed cloud models are thus preferred. In diffuse clouds, the physical conditions are relatively well known and the number of relevant molecular species is limited. Hence, detailed models that include the "complete" set of chemical reactions can be more reliably compared with observations.

II. GENERAL CONSIDERATIONS

Beginning with the earliest quantitative investigation of interstellar chemistry by Bates and Spitzer in 1951, there has been considerable controversy about the relative importance of gas phase versus catalytic processes on the surfaces of dust grains. Because of the clear success in understanding the formation of molecular hydrogen as due to surface chemistry, along with the absence of specific proposals for gas phase mechanisms except in a limited number of cases, most astronomers believed before 1973 that surface chemistry is somehow primarily responsible for interstellar molecule formation. A key problem was (and still is) how the molecules are ejected from the surface. Most species, though not H_2 , freeze at the temperatures expected for interstellar dust grains. In addition, the lack of predictability of surface reactions (especially in view of the unknown composition of the surface) made it seem unlikely that studies of interstellar chemistry could be put on a quantitative footing. However, recognition of the importance of reactions between positive ions and neutrals in dense clouds (Herbst and Klemperer 1973; Watson 1973, 1974) provided the basis for a quantitative, gas phase chemistry that has been explored in considerable detail in recent years. Reactions involving positive ions ordinarily are much more effective than those involving only neutrals because the former usually have no activation energy barriers when the reaction is exothermic. In addition, possible reactions that arise in dense clouds tend to be exothermic more often when a positive ion is involved. A cornerstone prediction of this "ion-molecule" scheme was that the ion HCO^+ should be abundant. At the time, its microwave frequencies were unknown. However, a strong, unidentified emission line ("X-ogen") near the estimated $J=1-0$ frequency of HCO^+ had been widely observed. First, detection of another emission line near the frequency expected for $J=1-0$ for $H^{13}CO^+$ (see Snyder et al. 1976) was convincing evidence that "X-ogen" should be identified with HCO^+ . Then, measurement of the frequency for HCO^+ in the laboratory (Woods et al. 1975) provided the definitive data for the identification.

Evidence that a gas phase chemistry oriented around positive ions dominates in dense clouds is by no means definitive, but is highly suggestive as a result of, for example:

- 1) the occurrence and the abundance of HCO^+ and N_2H^+ ,

- ii) the degree and the variation of the enhancement in the deuterium to hydrogen ratio in molecules,
- iii) the apparent fractionation of carbon isotopes in molecules in certain clouds,
- iv) the presence and abundance of HNC relative to HCN,
- v) the agreement between the predicted and deduced electron densities in dense clouds.

To see how it is that reactions involving ions can dominate for a gas in which the fractional ionization is only $\approx 10^{-8}$, consider the characteristic time scale associated with reactions on a grain surface. Based on the surface area of interstellar dust grains, the mean time for a specified particle in the gas to strike a grain -- the minimum time for it to be involved in a surface reaction -- is roughly $t_g \approx (10^{17}/n)$ sec. The minimum time for a specified gas particle to have its chemical form changed through ion-molecule reactions might be expected to be comparable to the time for it to be ionized directly by primary ionizing agent. In dense clouds, the agent presumably is high energy cosmic ray particles. The associated time scale $t_{di} \approx 10^{17}-10^{18}$ sec is much longer than t_g and probably even longer than the lifetime of the cloud. On this basis, ion-molecule reactions would ordinarily be unimportant. The key to the ion-molecule scheme, however, is the recognition that the direct ionization of hydrogen and helium can be transferred to the less abundant elements (e.g., C,N,O) with high efficiency. This then reduces the effective time scale t_i for ionization of C,N,O, etc. from t_{di} by a factor in the neighborhood of the abundance ratio ($\approx 10^4$). Thus $t_i \approx t_g$ when $n \approx 10^4 \text{ cm}^{-3}$ and an ion-stimulated chemistry might reasonably be competitive.

III. BASIC ASPECTS OF THE "ION-MOLECULE" SCHEME

Essentials of the ion-molecule scheme in dense clouds have been discussed in a number of reviews (e.g., Herbst and Klemperer 1976; Herbst 1978a; Watson 1976, 1978), and will not be duplicated here. The basic chain for the transfer of ionization is illustrated in Figure 3 of Watson (1978). Almost all ionizations of the chief component of the gas (H_2) produce H_3^+ , which frequently reacts with CO because of the high CO abundance to produce HCO^+ . Chemical reactions with CO and other species containing heavy elements ordinarily compete with electron recombination in the destruction of H_3^+ so that in fact an appreciable fraction of the ionizations of hydrogen are transferred to the less abundant, heavy elements. Ionization of helium plays a key role because the rate coefficients for reaction of He^+ with H and H_2 are anomalously small. To be neutralized, He^+ must then ionize molecules containing heavy elements and thus transfer its ionization. Even more important, the neutralization process of He^+ with diatomics frequently dissociates the diatomics. Free, reactive atoms and ions are thus produced from CO, N_2 , etc. which ordinarily are unreactive. This may be the means by which elements remain available for chemical reactions despite the general tendency toward depletion onto grains. Both CO and N_2 have vapor pressures which may be sufficient to prevent them from

freezing onto the grains. They then serve as "reservoirs" for atoms which are slowly being converted into other, less abundant species.

The electron density that is predicted as a result of this ionization (e.g., Watson 1978) is considerably smaller than would be the case if the gas were purely atomic. In an atomic gas, neutralization is due primarily to radiative electron recombination. In a molecular gas, molecular ions are likely to be the primary positive ions so that dissociative electron recombination will dominate the neutralization. This process has rate coefficients that typically are a factor of 10^4 - 10^5 larger than for radiative electron recombination with atomic ions. Even in a molecular gas the neutralization might, in principle, be controlled by radiative recombination if atoms of low ionization energy (e.g., Na, Ca, Si) are present in the gas at the level given by cosmic abundances (Oppenheimer and Dalgarno 1974). Positive ions are, however, neutralized upon collision with the negatively charged dust grains at a rate near $10^{-16} \text{ n s}^{-1}$ (Watson 1974). This rate ordinarily exceeds that for radiative recombination (rate coefficient $\approx 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) in dense clouds.

Representative examples of schemes to form simple molecules via ion-molecule processes include the reactions of H_3^+ with atomic O or N. In the first case, the product OH^+ will react successively with two H_2 molecules, capturing an H-atom in each reaction, to produce OH_3^+ . The OH_3^+ will then recombine dissociatively with an electron to produce H_2O and OH. The analogous reaction sequence for nitrogen illustrates the errors that can result from extrapolating information from measurements at 300 K to interstellar temperatures. Reaction of NH_3^+ with H_2 has a negligibly small rate coefficient at 300 K ($< 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) and it has been assumed the value would be even smaller at $T < 100$ K. Hence NH_4^+ , which could recombine dissociatively with an electron to produce ammonia, would not be produced in this manner. Alternative routes to ammonia are neutralization of the NH_3^+ by charge exchange with metal atoms and radiative association of NH_3^+ with H_2 to produce NH_5^+ which can then produce NH_3 through dissociative electron recombination. Very recently, however, the rate coefficient for $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$ was found to remain at about $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 100 K. The alternative routes are then slower. Another interesting example is the chemistry of C^+ . Although it cannot undergo an exchange reaction with H_2 , radiative association may be "unusually" rapid with a rate coefficient near $10^{-14} \text{ cm}^3 \text{ s}^{-1}$ (see article by E. Herbst in this Symposium). The CH_2^+ then reacts with H_2 to produce CH_3^+ which cannot capture an H-atom from H_2 . As discussed for NH_3^+ , charge exchange with a metal atom or radiative association with H_2 followed by electron recombination may then produce CH_3 and CH_4 .

Specific proposals have been made within the "ion-molecule" scheme for the formation of most molecules of "intermediate" complexity. Various meaningful tests can be performed. A quantitative understanding of these formation processes is clearly desirable as a basis for examining the abundances of the most complex molecules. Examples of proposals for species of particular note are the reaction mechanisms involving C_2H , H_2CO and HCN/HNC , all of which are summarized in Watson (1976)

among other locations. The relatively high abundance of C_2H was predicted in advance of its detection and the reactions that are involved may be essential to producing the carbon chain molecules. Formaldehyde is widely observed in interstellar clouds under nearly all physical conditions. Understanding its formation processes has seemed especially important as an indication of the ability of gas phase schemes to produce the more complex molecules. In attempting to formulate quantitative tests of proposed reaction schemes, we (Watson, Crutcher and Dickel 1975) argued that all proposed formation schemes for H_2CO should also produce a high abundance of HDCO which probably would be in conflict with the failure to detect the $l_{11}-l_{10}$ transition of this species. A considerable amount of interpretation, along with a slightly erroneous laboratory frequency, was involved. The detection of HDCO at millimeter wavelengths (Langer, Frerking, Linke and Wilson 1979) shows that the abundance of HDCO actually is not in conflict with the proposed reaction mechanisms for H_2CO (esp. $CH_3 + O \rightarrow H_2CO + H$). The high abundance of HNC was immediately recognized as a likely consequence of specific ion-molecule reactions and more generally as a strong indication that interstellar molecules are produced by non-(thermodynamic) equilibrium processes in the gas phase. HCN and HNC are expected to be produced by the dissociative electron recombination of $HCNH^+$ (see Herbst 1978b for a detailed discussion of the dissociation) which is a result of $C^+ + NH_3$. Since HCN and HNC are also destroyed through reaction with C^+ , a model-independent (though steady-state) result is $([HCN] + [HNC])/NH_3 \lesssim 0.6$ (e.g., Watson 1976). Though there are uncertainties in deducing the observed abundances, observations are considered to be compatible with this ratio. This predicted ratio will be altered if the fractional abundances of NH_3 and H_2O , which react with C_2N^+ to produce HCN/HNC (Schiff and Bohme 1979), exceed about 10^{-5} . Recently there has been some debate about the likelihood that HCN and HNC should both be produced in the recombination of the molecular ion that results from $C^+ + NH_3$. R. D. Brown (1977) noted that the structure H_2NC^+ may reasonably be expected to be metastable and that it should be formed preferentially because to do otherwise would involve breaking the N-H bonds already present in the reactant ammonia. In this case, little HCN might be expected to result from the electron recombination. However, subsequent molecular orbital calculations (Conrad and Schaefer 1978) indicate that in fact there is no energy barrier for H_2NC^+ to rearrange into the configuration of lower energy $HNCH^+$.

IV. DETAILED NUMERICAL MODELS

Since the idealized goal of interstellar chemistry is to understand all molecular abundances, it is certainly appropriate to attempt to construct detailed numerical models that include the formation and destruction processes for as many species as possible. Most efforts have considered only the small molecules ($\lesssim 4$ atoms). Herbst and Klemperer (1973) constructed the first such model for dense clouds that includes ion-molecule reactions. A number of investigators have refined and extended the original model. More extensive reaction networks have been considered (Mitchell, Ginsburg and Kuntz 1978), along with the time

dependence involved for the reactions to reach steady-state under fixed physical conditions (Prasad and Huntress 1979; Suzuki 1979) and including the effects of depletion onto dust grains in a specific approximation (Iglesias 1977). The time dependent calculations do illustrate that steady-state for the chemical reactions alone is achieved in about 10^6 years under representative conditions for dense clouds. As one might expect from the comparison of t_g with t_i in Section II, the effects of depletion are likely to become important in approximately the same time scale (see Figure 4 of Iglesias 1977). Observations (Wootten et al. 1978) indicate that fractional molecular abundances do decrease (by a factor of ≈ 100 in the sample considered) as gas density increases and hence as t_g decreases. Model calculations that also attempt to simulate changes in the cloud (especially collapse) involve a time dependence in the external physical conditions (density, temperature) are also available (Suzuki et al. 1976; Gerola and Glassgold 1978). The differences between these calculations already indicate some of the uncertainties that arise in applying the models to interstellar clouds. In addition, for models containing only the simplest molecules (≤ 3 atoms) perhaps 2/3 of the rate coefficients have not been measured in the laboratory. Only a few have been measured at temperatures below 300 K. Due to depletion in even the diffuse phase of the cloud, the initial abundances of the elements in gaseous form (especially for the metals) are also a major problem.

V. FORMATION OF COMPLEX MOLECULES

Understanding the formation of the complex molecules is certainly the greatest challenge in interstellar chemistry. It is also fraught with uncertainty because a number of steps are needed to convert individual atoms into molecules. The rate coefficients and branching ratios for these are even more poorly known than for the smaller molecules which were discussed in the previous sections.

In the past year or so there have been a number of studies which indicate that at least a qualitative understanding of the chemistry of the complex molecules may be near. This optimism is due primarily to progress in two general areas. (i) Extensive studies have been performed for reactions of the type,



Here AB^+ ordinarily will be more complex than AX^+ or BY so that the overall effect tends to be the step-by-step conversion of simpler to more complex species. There has been speculation since the earliest studies of ion-molecule chemistry that such processes might lead to the more complex molecules. Neutralization by charge exchange with metals or by dissociative electron recombination might be expected to convert the ions into the observed neutrals. In the latter case the products are uncertain and the neutral molecular complex might break up into two smaller species rather than into a large molecule. At the time of the

earlier speculations, almost no laboratory data were available on reactions of the type in equation (1) when larger molecules are involved. Laboratory investigations have now begun to provide information on these reactions (Huntress 1977; Smith and Adams 1977; Freeman, Harland and McEwan 1979; Schiff and Bohme 1979). (ii) The second major area of progress is in the radiative association of larger molecules. Studies (Arnold 1977; Smith and Adams 1978a) show that the rate coefficients for 3-body association involving an ion,



increase rapidly (frequently by a factor of 100 or so) as the temperature is decreased from 300 K to 100 K. The increase is interpreted as due to the increased lifetime of the intermediate, excited complex $(AB^+)^*$. The lifetime of this complex can be related to the probability that the complex $(AB^+)^*$ will de-excite in the interstellar medium by emission of radiation. Though there is some uncertainty in converting the laboratory data into radiative association rates and it is unclear whether the temperature dependence observed above 100 K is completely accurate down to 20 K, it does seem clear that at least some radiative association rates are much more rapid than was previously expected. For example, Smith and Adams (1978a) deduce the following rate coefficients (cm^3s^{-1}) at 50 K: $\text{CH}_3^+ + \text{H}_2^+$ (4×10^{-13}), $\text{CH}_3^+ + \text{CO}$ (3.5×10^{-12}), $\text{CH}_3^+ + \text{H}_2\text{O}$ ($\lambda 2 \times 10^{-9}$) and $\text{CH}_3^+ + \text{NH}_3$ ($\lambda 4 \times 10^{-10}$). That is, the derived radiative association rates are in some cases near the kinetic collision rate. Herbst (1976) studied radiative association involving molecules from a theoretical viewpoint and will present refinements of his work in light of the laboratory data at this Symposium.

Formation of complex molecules has been discussed within the context of the recent laboratory data by a number of investigators (e.g., Smith and Adams 1978b; Walmsley, Winnewisser and Toelle 1979; Schiff and Bohme 1979; Huntress and Mitchell 1979). Because this work is very recent and much of it is being presented at this Symposium by the authors, I will not go into further detail.

VI. ISOTOPE FRACTIONATION

Studies of the fractionation of deuterium in molecules is perhaps the area where ion-molecule chemistry in dense clouds has been utilized most quantitatively to obtain information of general astronomical interest. Consideration of very different reactions also suggests the $^{13}\text{C}/^{12}\text{C}$ ratio in molecules may be influenced by chemical fractionation.

In the case of deuterium, reactions of the type,



tend to take deuterium from the HD "reservoir" and concentrate it in other molecules. Reaction (3) is known to have a large rate coefficient when $AH^+ = \text{CH}_3^+$ and H_3^+ , but apparently not for N_2H^+ or HCO^+ . If reaction

(3) is to be effective in enhancing the (D/H) ratio in AH^+ , it must compete with destruction of AH^+ by other processes. Specifically, it must compete with dissociative electron recombination and with reactions involving other molecular species. This provides an upper limit to the abundance of electrons and of the other species from the observed (D/H) of the molecule. Detection of DCO^+ (Hollis et al. 1976) and N_2D^+ (Snyder et al. 1977) made possible the most reliable application of this diagnostic technique because the relevant reactions are best understood for these species. From the initial detection of DCO^+ , upper limits near 10^{-8} were deduced for the electron densities in cool clouds (Watson 1977). More extensive surveys and more refined studies of the radiative transfer confirm this evidence for a low electron density in cool interstellar clouds (Guelin et al. 1977; Watson, Snyder and Hollis 1978; Langer et al. 1978).

Laboratory data on the rate coefficients for dissociative electron recombination of H_3^+ at low energies (≈ 0.01 eV; Auerbach et al. 1977), as well as on isotopic forms of H_3^+ (McGowan et al. 1979) and of N_2H^+ (Mul and McGowan 1979) have been especially valuable in reducing substantially the uncertainties in the chemistry.

The isotope exchange of equation (3), is "driven" by zero point energy differences which give an exothermicity of $\Delta E/k \approx 200-400$ K depending upon the particular reaction. Although other factors such as electron density also contribute to determining the degree of fractionation, the temperature is not negligible in comparison with $\Delta E/k$ and one might therefore expect a temperature dependence to be present in the observational data. A recent study of the (DNC/HNC) ratio for 18 clouds finds a clear temperature dependence with a derived value $\Delta E/k = 240 \text{ K} \pm 60$ for this species (Snell and Wootten 1979).

Fractionation of carbon isotopes in molecules can occur directly or indirectly as a result of the exchange (Watson, Anicich and Huntress 1976),



It was shown analytically that the $^{13}CO/^{12}CO$ ratio will be enhanced over the $^{13}C/^{12}C$ ratio of the gas if most carbon is in atomic form, but not when most carbon is in molecular form (primarily CO). Secondly, it was shown analytically that preferential depletion of carbon-bearing molecules other than CO onto grains might lead to an overall enhancement of ^{13}C in the gas. The effect of equation (4) has been investigated further in detailed cloud models by Langer (1977) and Liszt (1978). The latter study finds that the overall enhancement due to depletion is not great for the particular assumptions of the models that are involved.

A striking observational example of the first fractionation effect for carbon isotopes apparently occurs in the cloud L134 (Dickman et al. 1977). This interpretation is supported by more detailed studies of

the uncertainties due to radiative transfer effects (Dickman, McCutcheon and Shuter 1979; Langer, Goldsmith, Carlson and Wilson 1980).

VII. SHOCKS

There is evidence, especially from the infrared emission by H₂ molecules, that shocks are present to at least some degree in certain dense clouds. Broad molecular lines and "unusually" high abundances have led to proposals that in the Orion cloud the observed SiO and OSC (Lada, Oppenheimer and Hartquist 1978) as well as the H₂O (Elitzur 1979) are formed in the hot gas behind a shock front. These investigators, as well as Iglesias and Silk (1978), have performed detailed computations to assess the contribution by shocks to molecular abundances in dense clouds. Endothermic chemical reactions, which ordinarily are unimportant at the low temperatures in dense clouds, play a key role. Shocks may also contribute appreciably to molecular abundances in diffuse clouds (Elitzur and Watson 1978).

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DISCUSSION FOLLOWING WATSON

Glassgold: I was tremendously impressed by the success of the ion-molecule chemistry which you so well described despite the fact that there are relatively few abundance determinations in dense clouds. The recent results from Texas point up the usefulness of absolute abundance determinations, and I urge the observers here to devote some effort in this direction. I would like to cite two important applications requiring better molecular abundance determinations. The first is the estimation of cloud masses, which requires an accurate value for the $^{13}\text{CO}/\text{H}_2$ ratio. The second is the problem of understanding the thermal properties of dust clouds. Until the abundances of the major molecular coolants have been determined, the temperatures of these clouds cannot be understood.

Kutner: Absolute abundances are still hard to measure, but are coming within the realm of possibility. In the meantime much quantitative information can be obtained from studies of certain relative abundances, and how they vary with physical conditions such as temperature, density and ionization level.

Scoville: Are there any areas in which there is an apparent contradiction between the observed interstellar chemistry and ion-molecule gas-phase theory?

Watson: I know of none in the "dense cloud" regime, though I expect that Dalgarno will mention one in "diffuse cloud" chemistry.

Scoville: Is that due to lack of quantitative data?

Watson: It helps.

Kutner: There is a large range of objects that we would classify as cool, dense and dark, but into which the UV will still penetrate, depending on the grain albedo and phase function. Is there an effort being made to model the chemistry in such intermediate regions?

Watson: There are calculations by Langer and Glassgold in Ap. J.

Elmegreen: It is possible that charged grains play a fairly important role in determining the ionization fractions in dense clouds because they will neutralize the metallic ions at a faster rate than radiative recombination for electron fractions less than about 10^{-7} . Charged grains also may add considerably to the viscous coupling between a magnetic field and the neutral molecules, and may dominate this coupling at electron fractions less than about 5×10^{-8} . These numbers depend on the grain size and abundance, but they should be representative of typical conditions.

Watson: The contribution of grains to the recombination has been noted several times in the literature.

Gold: Gas-phase build-up of molecules would lead to a very different dependence of abundance on atomic number from the process of association on grains. Do we not have enough statistical information of abundances to decide which process is more important?

Watson: It is not clear to me that there would necessarily be a very different dependence of abundance on atomic number, given our lack of knowledge of grain processes and of the physical conditions under which gas-phase reactions proceed.

Allamandola: You make the point that any serious consideration of

the contribution of grain reactions to the overall cloud chemistry must first overcome the problem of getting the molecules which have stuck to the grains back off into the gas-phase. In our experiments at Leiden, we are duplicating, as far as possible, molecular mantles at 10 K and subjecting them to ultra-violet radiation. We have found that radicals are generated and stored in samples which have undergone irradiation. When we allow an irradiated sample to undergo a very small rise in temperature of 1 to 5 K, we see visible emission due to the radicals reacting in the solid in a process similar to radiative recombination. This implies that molecules are formed *in the mantle* in excited states (5eV is typical) and are thus an internal energy source. Some of this energy is apparently converted to heat because we observe a substantial vapor pressure increase in the range 15-22 K in irradiated samples as compared to non-irradiated ones. Thus we feel that a mild warming event of only a few degrees can vaporize a small portion of the mantle and inject those molecules into the gas-phase.

Watson: One must keep in mind that a high efficiency is required in order that this process eject a significant fraction of the atoms that stick to a grain in dense clouds. At the *edge* of a cloud, the flux of UV photons due to the galactic background is in the neighbourhood of $10^7 \text{cm}^{-2} \text{s}^{-1}$. The flux of C,N,O, etc. atoms is $10^4 \text{cm}^{-2} \text{s}^{-1}$ at a density of 10^4 particles cm^{-3} . However, the UV radiation presumably is reduced by many orders of magnitude in the interiors of dense clouds.

Gold: Can cosmic ray evaporation from grains not account for an adequate re-supply to the gas of molecules formed on grains?

Watson: Various cosmic ray evaporation processes have been investigated in great detail (some by me). At best, they might do the job in the lower density clouds (≤ 100 particles cm^{-3}).

Greenberg: The evidence for accretion on grains has been available for a long time in the *observational* fact that the wavelength dependence of both extinction and polarization in dense clouds shows larger than normal grains.

Watson: True, but data from the study of grains is not sensitive to fractional depletions exceeding perhaps 2/3, whereas the radio observations suggest that less than one percent of the "heavy" elements remain in the gas at high densities.

Greenberg: If you believe that grain accretion takes place, as you implied when you presented results based on gas-phase reactions *including* grain accretion, then I do not see how you can justify the ion-molecule reaction schemes you suggested. The accretion time scale at $n=10^4 \text{cm}^{-3}$ is $\sim 10^6$ years, i.e. about equal to the free fall time scale, and if the free fall time scale is a substantial underestimate of cloud lifetimes, then there should be a *very* small number of molecules in 10^4 density clouds. The answer which I have proposed is that, as a result of rather small energy impulses to the grains (an increase in temperature by about 10-20 K), the energy stored in them as radicals can be released, and lead to partial or complete evaporation of the grain mantle, which includes all sorts of molecules.

Watson: I readily acknowledge (even pointed out in my lecture) that the gas-grain interaction is a major problem. However, the two time scales are roughly equal at densities of 10^4cm^{-3} , so it is not

unreasonable to proceed in the expectation that order-of-magnitude results can be achieved from gas-phase chemistry (the time scale for gas-phase chemistry is reduced by depletion, also). If the effect of grains is non-selective depletion, one might reasonably expect (very roughly) just an overall reduction of absolute abundances, as suggested by the calculations of Iglesias (1977). The comparison between observations and the predictions of gas-phase chemistry for small molecules and molecular ions certainly indicates that the present approach is reasonable.