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by

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ABSTRACT

Reactions between atoms and ions of the interstellar medium and vibrationally excited molecular hydrogen are shown to produce a specific set of molecules. Molecules such as CO and CN can readily be produced in abundances greater than those of corresponding hydrides. When quantified in a simple manner the equilibrium density of molecules compares well with the observed values for ζ Oph.

I. INTRODUCTION

We have recently discussed the role played by internal energy in the ion-molecule reaction $C^+ + H_2 \rightarrow$ products, and the relevance of this reaction to the interstellar medium (Stecher and Williams 1972a). We have argued on the basis of many similar examples that sufficient molecular vibrational energy can overcome endothermicity and that such reactions then proceed with high rate. Our purpose here is to discuss in a similar way the chemical exchange reactions (sometimes called metathetical reactions). We are then able to list a set of many reactions which will be expected to proceed with high rates in the interstellar medium. This list predicts a set of products which ought to be present in the interstellar medium, and also identifies some molecules which are not formed by this mechanism. We quantify this mechanism with a crude choice of values for the parameters involved, and compare the predicted abundances with those observed in the direction of ζ Oph.

II. INTERNAL ENERGY IN CHEMICAL EXCHANGE REACTIONS

The relative translational energy in a neutral chemical exchange reaction has traditionally been considered the important factor which may cause the reaction to proceed, i.e. it may assist the reactants in overcoming the activation energy barrier nearly always present. The significance of the vibrational energy in chemical exchange reactions has, however, been emphasized in several recent experiments.

For example, Jaffe and Anderson (1968) have shown that vibrational energy is essential to bring about a reaction between HI molecules. There is evidence (Parker and Pimentel 1969, Polanyi and Tardy 1969) that in the endothermic reaction between H and HF the vibrational energy of the HF molecules is the driving energy. Other examples are given by Spicer and Rabinovitch (1970). Theoretical investigations by Polanyi and collaborators also place emphasis on the vibrational energy of the participant molecules. Their work suggests that vibrational energy is particularly effective in forcing otherwise endothermic reactions to proceed (Polanyi and Wong 1969, Mok and Polanyi 1969).

Let us consider an example of such a reaction which has relevance to the interstellar medium. The endothermicity in the reaction $O + H_2 \rightarrow OH + H$ is 0.082 eV (Wilkinson 1963, Gaydon 1968). This reaction has been suggested by Carroll and Salpeter (1966) as the formation mechanism for OH in the interstellar medium. Assuming that loss of OH occurs predominantly in the inverse reaction then Carroll and Salpeter found that in short lived high temperature periods - during which the rates are high - amounts of OH consistent with the observations were formed. However, photodissociation of OH certainly occurs, directly, and also by predissociations. A mean life in the typical interstellar field is ~ 10^{11}s (Stecher and Williams 1966). Dalgarno and McCray (1972) have also pointed out the possibility of the fast reaction $C^+ + OH$ as a loss mechanism for OH. Consequently, the reaction cannot supply enough interstellar OH if translational energy is the driving energy. However, in the light of the discussion given above, we expect that $O + H_2$ reaction will proceed if H_2 is vibrationally excited (written H_2^*)with v" ≥ 1, for this level is energetic enough to overcome the measured activation energy of 0.44 eV (Wong and Potter 1965, Westenberg and de Haas 1967) plus the endothermicity. We now assume that this is the case, and that the reactions with H_2^* proceeds with a rate constant $\sim 10^{-11} cm^3 s^{-1}$ comparable with the "pre-exponential factor" inferred from experiments listed which are driven by kinetic energy. Since higher vibrational energy usually provides a bigger reaction rate, we are here making a conservative assumption.

Though the discussion above is concerned with O reacting with H_2^* the situation for other atoms is not very different. Metathetical reactions usually involve an activation energy rather less than 1/2 eV (e.g. Kaufman 1969). The endothermicity may be calculated from the binding energies of the molecules involved. The assumption is that if enough energy is inserted in the form of vibration in H_2 then the reaction proceeds with a rate coefficient typically $\sim 10^{-11} cm^3 s^{-1}$, (Kaufman 1969).

III. THE SCHEME FOR DIATOMIC MOLECULE PRODUCTION

We have recently estimated the abundance of vibrationally excited H_2 in interstellar clouds (Stecher and Williams 1972b). The majority of absorptions in the Lyman and Werner bands cascade down into highly excited vibrational levels of the groundstate. Because H_2 is homonuclear, these levels have long radiative lifetimes, $\sim 10^6$s (Dalgarno, private communication), and we calculate that $\sim 0.1\%$ of H_2 is in some excited vibrational level in typical clouds of H_2. In Table I we show the fraction $\alpha_{v''}$ of molecules in each vibrational level allowing for excitation in the Lyman and Werner bands and vibrational relaxation in the ground state. This table was computed using the data of Allison and Dalgarno (1969) and Cartwright and Drapatz (1970).

Since according to the discussion above, H_2^* is able to react with atoms and ions with high rates, we draw up a set of allowed reactions between H_2^* and the most abundant atoms and ions in the interstellar medium. These are C^+, O, N, Si^+, Mg^+, S^+. These reactions are presented in Table II. The primary set of reactions is of H_2^* with each of the atoms and ions. This set gives rise to hydrides and hydride ions, which in secondary reactions with the atoms and ions present produce a great variety of subsequent diatomic molecules and molecular ions. Further reactions between these second stage products are possible, but their products are expected to be down in abundance by a large factor. This assumption is later justified by numerical work. Apart from the primary reactions of O and N atoms with H_2^*, all other reactions are of ion-molecule form and are expected to have very high rates (McDaniel et al. 1970). The products of these primary reactions may be formed in excited vibrational levels. In many cases it is extremely likely (Kuntz et al. 1966). However, these product molecules all possess dipole moments, and so vibrational relaxation will be relatively rapid. Reactions between neutrals, with very few exceptions, (Williams 1971, Kaufman 1969) involve activation energies which effectively prevent these reactions occurring with appreciable rate at the temperatures of interstellar clouds. We therefore ignore neutral-neutral reactions, apart from the primary reactions with H_2^*.

One of the most interesting features of the set of reactions in Table II is that it gives an immediate prediction of which molecules are produced, and which are not produced, by these mechanisms. The criterion is that all the reactions listed shall be exothermic. Endothermic reactions will have rate coefficients smaller by about four orders of magnitude in interstellar conditions. Exothermicity was ensured by reference to the tables of Wilkinson (1963) and Gaydon (1968). Reactions which do not appear in Table II have been omitted by virtue of their endothermicity. We list in Table III the obvious absentees from the products. An observation of any of these molecules or ions in the interstellar medium would immediately invoke a different mechanism. The allowed products can be seen from Table II. In Table III some of the neutral absentees could be formed by recombinations of electrons with suitable ions which are present. These molecules are noted in the table. However, if dissociative recombination occurs it will be a much more rapid process.

Typically, it has a rate coefficient ~ $10^{-7} cm^3 s^{-1}$ (Bardsley and Biondi 1970). The most favorable theoretical rate for recombination (including dielectronic recombination) is ~ $10^{-10} cm^3 s^{-1}$, but rates of this magnitude have not yet been found. According to Hasted (1964) it is likely that recombination rates are two orders of magnitude less than this. We conclude that neutral molecules are unlikely to be formed by ion-recombination with electrons, and that any interstellar molecular production theory based on this assumption is in conflict with present laboratory measurements.

The gratifying result of the qualitative inspection of these equations is that those diatomic molecules which have been observed in the interstellar medium are, indeed, formed by the processes described here.

IV. NUMERICAL PREDICTIONS OF MOLECULAR ABUNDANCES

If one can assign suitable rate coefficients for the reactions in Table II and also for all relevant loss mechanisms, then one may, on the assumption of dynamical equilibrium, calculate equilibrium abundances. The loss mechanisms for hydrides, of course, involve the secondary reactions, but all molecules are subject to photodissociation, neutrals also to photoionization if their ionization potential is less than 13.6 eV, and ions are also subject to dissociative recombination with electrons. Photodissociation, photoionization, and the amount of vibrational excitation all depend on the interstellar radiation field which varies greatly from place to place.

It seems appropriate to calculate molecular abundances for a specific situation in the interstellar medium so that a comparison with observation may be made. The most careful and complete observations available to us at this time are those which were made in the direction of ζ Oph (Herbig 1968, Smith and Stecher 1971, Smith 1972). We, therefore, attempt to define this situation so that we may compute the appropriate parameters.

The star ζ Oph is a bright early type star (O 9.5V). We shall represent its spectrum in the relevent wavelength regions by that of a 30,000°K black body diluted by a factor 10^{-14}. This implies that we are concerned with a region some parsecs away from the star. Herbig's detailed observations of ζ Oph coupled with Stecher's (1968) measurement of Lyα in this direction led Herbig to suggest that the molecules were found in a relatively dense sheet ($n(H) \sim 10^2$-10^3 cm^{-3}) of gas in which the extinction was about 1 mag. Even if the situation were dynamically steady (which it is not) then we would expect on the basis of H_2 production theories considerable amounts of H_2 in clouds of this density (Hollenbach, Werner and Salpeter 1971). In fact, ζ Oph is moving at high velocity relative to its local environment (Blaauw 1961) and clouds of density ~ 10^2cm^{-3} in a less intense radiation field will certainly contain much H_2. In the computations of photodissociation, photoionization, and $n(H_2^*)$ we assume the radiation field stated above, which is equivalent to

$\sim 10^6$ photons $cm^{-2}s^{-1}Å^{-1}$ at 1000Å and 5 x 10^5 photons $cm^{-2}s^{-1}Å^{-1}$ at 3000Å. Inside the cloud extinction reduces these fluxes by a factor of 5 at 1000Å and factor of 3/2 at 3000Å, using Stecher's (1969) extinction measurements. This field, including extinction, gives an excitation rate from X, v" = 0, excluding dissociation, of $\beta = 10^{-9}s^{-1}$.

We now discuss the various parameters and the values adopted.

(a) Reactions of H_2^* with neutral atoms.

The case of O + H_2^* has been discussed already. We adopt a rate coefficient of 10^{-11} cm^3s^{-1} for v" ≥ 1, which is probably a conservative estimate. No similar measurement involving N appears to be available, but other reactions between N and O with the same molecules have similar rates. We, therefore, adopt $10^{-11}cm^{-3}s^{-1}$ for the reaction H_2^* + N, which becomes exothermic for v" ≥ 4.

(b) Reactions of H_2^* with ions.

We have discussed H_2^* + C^+ elsewhere (Stecher and Williams 1972a). The rate coefficients used were based on a measured cross section of $10^{-16}cm^2$ (Maier 1966), and the rate coefficients adopted were $10^{-11}cm^3s^{-1}$. It is possible that this is an underestimate. The measurements were performed at relative energies of several volts to overcome the endothermicity of 0.4 eV. If this problem is removed by the use of internal energy, then the reactants can approach and react at much lower velocities, at which the usual polarization forces dominate (Gioumousis and Stevenson 1958).

One could argue that a more appropriate value would be one or two orders of magnitude larger. However, we retain the values of $10^{-11} cm^3 s^{-1}$ as a conservative estimate. Measurements for Si^+ and S^+ have not been performed. We adopt the same value for the analogous reactions when they are made exothermic by the insertion of sufficient vibrational energy. Again, this may be an underestimate.

(c) Other ion - molecule reactions.

These reactions are almost invariably fast when they occur, i.e. when they are exothermic. Many examples are available (McDaniel et al. 1970, Ferguson et al. 1969) and nearly all have rate coefficients ~ $10^{-9} cm^3 s^{-1}$. There is little direct evidence concerning the actual reactions involved here. We adopt rate coefficients of $10^{-9} cm^3 s^{-1}$ for all ion-molecule reactions, excluding those discussed in (b).

(d) Dissociative Recombination

As mentioned earlier, this process is extremely rapid when it occurs. Values as great at $10^{-6} cm^3 s^{-1}$ are measured for large complex ions bound by polarization forces. But values ~$10^{-7} cm^3 s^{-1}$ seem appropriate for diatomic ions. When neither atom is hydrogen, the complexity of states make it extremely probable that there is a favorable crossing of a neutral repulsive potential curve with the ground state curve of the ion. Thus, the rates will be large. For hydrides the situation is simpler, and the existence of suitable crossings is not predictable. However, unpublished calculations by Krauss indicate that there is a suitable crossing in CH^+ + e so that the rate for dissociative recombination will be high. In the absence of further information we assume all molecular ions in this work dissociatively recombine with a rate coefficient of $10^{-7} cm^3 s^{-1}$.

(e) Photoionization.

Neutral molecules will be readily photoionized if their ionization potentials are appreciably less than 13.6eV. We choose a cut-off at 13.0 eV. We assume that near threshold the cross sections are all $\sim 10^{-17} cm^2$. The important contributors are those listed in Table IV.

(f) Photodissociation.

The photodissociation cross sections for the molecules involved are poorly known, if at all. Most effort has been applied to the CH molecule in recent years, and the discovery of many predissociated levels (Herzberg and Johns 1969) has led to a great reduction in the lifetime of CH against photodissociation in the interstellar medium (Hesser and Lutz 1970). Recent estimates by Stief et al. (1972) show that a strongly bound molecule like CO may still have a fairly short lifetime in the interstellar medium depending on the photon efficiency. None of the calculations are directly applicable to the present case. Correction must be made for the stronger radiation field we use and the mean extinction. We have made crude estimates of photodissociation taking account of electronic structure and states where known. We have adopted two rates; fast, $10^{-8}s^{-1}$, and slow, $10^{-9}s^{-1}$, as shown in Table V.

(g) The abundances assumed were the usual cosmic values (Allen 1963). We have further assumed $n(H_2) = n(H)$, so that the abundances are calculated relative to the total density of $n = n(H) + 2n(H_2)$. We have adopted $n(e) = 6 \times 10^{-4}n$ which is equal to that of $n(C^+)$, and $n(H^+) = 3 \times 10^{-4}$ together. We expect a contribution to both e and H^+ abundances from direct photoionization of H_2^* for $v'' \leq 4$ which is permissible for radiation for which $\lambda > 912Å$ (Stecher and Williams 1972c).

V. RESULTS AND DISCUSSION

We present the equilibrium abundances of all the product molecules at a specified density of H_2 of $10^2 cm^{-3}$ in Table VI and in Figure I we show the abundance of the observed molecules as a function of $n(H_2)$. Clearly, the choice of the parameters involved is difficult and, at times, arbitrary. Hence, absolute reliance cannot be placed on the individual abundances. However, the figure shows results which are quite striking in their behavior. For the first time, here is a mechanism which readily produces molecules XY in greater abundance than molecules XH, where X and Y are not H. The ratios between observed molecules are in harmony with the observations, remarkably so, considering the crudeness of the parameters. For example the ratio of [CO]/[CH] observed is about 40. The figure leads to a ratio on the order of 10 over a wide range of densities. The measured [CH]/[CN] ratio is about 5.

For densities less than 500 cm^{-3} we calculate this ratio to be between 1 and 5. The measured [CH]/[CH^+] ratio is on the order of unity, consistent with our calculations.

The absolute values of the column densities may be calculated using Stecher's (1968) column density for ζ Oph as a normalizing observation. Calculations are presented in Table VII. There is remarkable agreement between some theory and observations at the density of $n(H_2) = 10^2 cm^{-3}$, but a discrepancy for CO. Slightly higher densities would improve the agreement. Insufficient CO is produced, by more than a factor of 10. The source of this discrepancy may lie either in the choice of the photodissociation rate, or in ignorance of a particularly favorable production mechanism. A new measurement of CO photodissociation would be valuable. Within the crudity of the present work, this discrepancy is not too serious. The amount of OH calculated is above the upper limit set by Herbig. This is not a serious objection for several reasons: OH has yet to be seen in the UV though its presence is well established, there appears to be some observational problem; it is possible that OH is particularly vulnerable to third stage reactions such as $H_2^* + OH \rightarrow H_2O + H$ which should proceed with a rate coefficient $\sim 10^{-11}$ $cm^3 s^{-1}$ (Dixon-Lewis, et al. 1966). We have not included these third stage reactions in the computations, for lack of data on comparable reactions. However, the reaction referred to here should constitute a significant loss rate for OH and an interesting source of H_2O in the interstellar medium. There are some other reactions of a similar nature which may also be fast, but which we have not included in the production scheme because of lack of information concerning the complete set of an logous reactions. It is possible that NH and H_2^* react to form NH_2 similar to OH and H_2^*. Ion-molecule reactions more complicated than those considered here may also occur, for example $CH^+ + H_2 \rightarrow CH_2^+ + H$ is known to be fairly fast (McDaniel et.al, 1970) Thus, although we have limited our discussion to diatomic molecules and ions, it seems quite likely that triatomics will also evolve naturally. However, we need more information before we can include them in our computations.

We have chosen to examine the situation in the direction of ζ Oph where we believe the radiation is intense. It is interesting to consider the effect of reducing the radiation intensity corresponding to other regions in the interstellar medium. As far as neutral molecules are concerned their loss is dominated by photodissociation, and their production depends directly or indirectly on the abundance of H_2^* which in turn is dependent on the radiation field. Hence, rather surprisingly, the abundance of neutral molecules formed by these mechanisms is not expected to vary greatly with radiation field. However, the dominant loss mechanism for molecular ions is dissociative recombination, and the electron abundance is fairly insensitive to radiation intensity, over a wide range. Hence the abundance of molecular ions should be roughly proportional to the radiation intensity. These simple arguments may be used as a tool to measure the interstellar radiation field when the rates are more precisely known.

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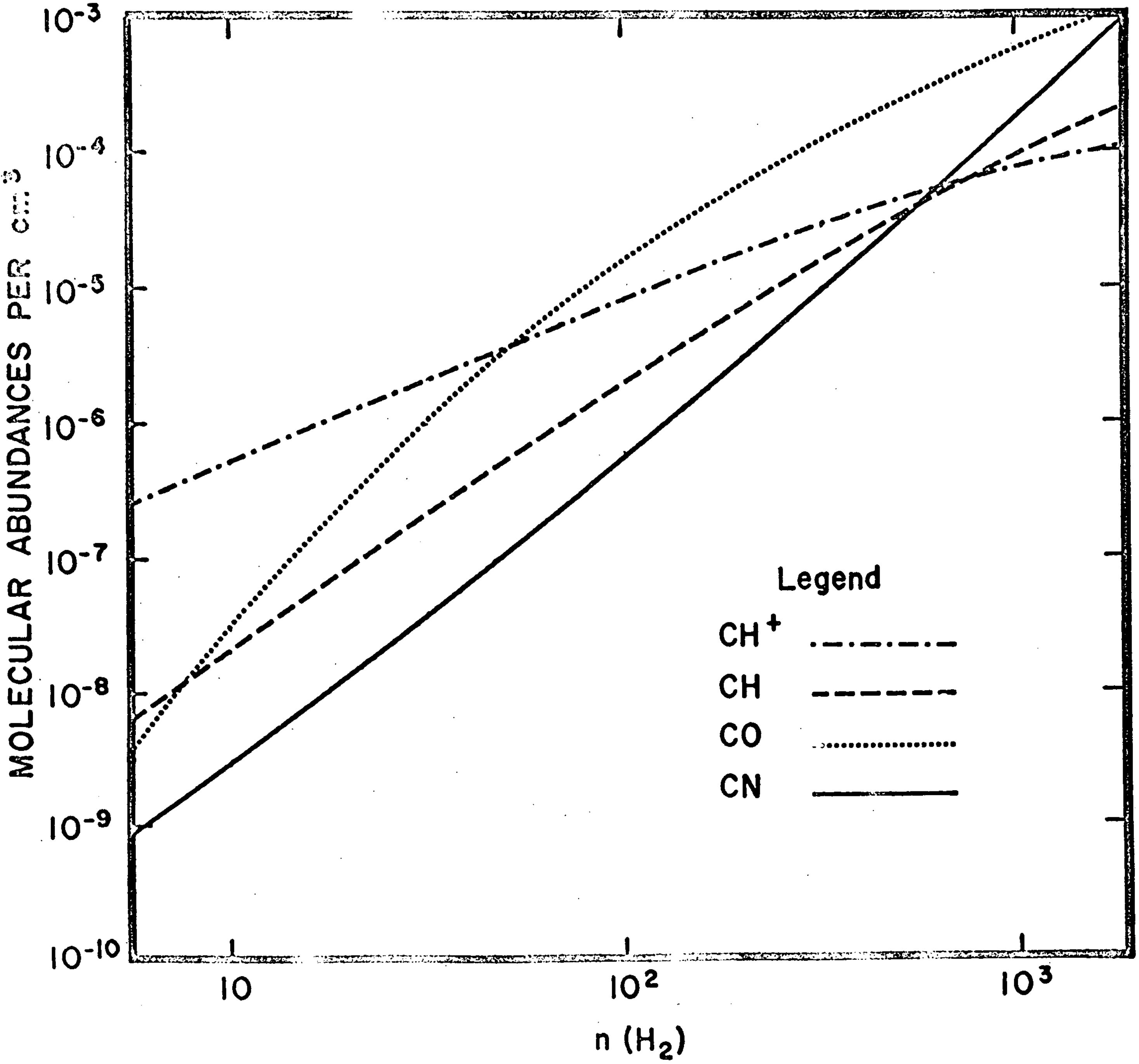
LEGEND FOR FIGURE

Calculated abundances per cm^3 for the molecules CH, CH^+, CO, CN observed in the direction of ζ Oph, as a function of $n(H_2)$.



MOLECULAR ABUNDANCES PER cm^{-3}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10
10^2
10^3
n (H_2)
Legend
CH^+ –·–·–·–
CH – – – – –
CO ··········
CN ———

TABLE I

Equilibrium fraction of H_2 in each excited vibrational level, in terms of the excitation rate β (s^{-1}). In our model we set $\beta = 10^{-9} s^{-1}$

Vibrational level	$\frac{10^{-6}}{\beta}$ x Fraction of H_2 in level
1	0.994
2	0.467
3	0.288
4	0.198
5	0.142
6	0.105
7	0.079
8	0.061
9	0.048
10	0.038
11	0.032
12	0.028
13	0.024
14	0.021

TABLE II

Exothermic Reactions

Primary Reactions

$H_2^*(v'' \geq 1) + C^+ \rightarrow CH^+ + H$	$H_2^*(v'' \geq 1) + O \rightarrow OH + H$
$H_2^*(v'' \geq 9) + C^+ \rightarrow CH + H^+$	$H_2^*(v'' \geq 4) + N \rightarrow NH + H$
$H_2^*(v'' \geq 6) + Mg^+ \rightarrow MgH^+ H$	
$H_2^*(v'' \geq 3) + Si^+ \rightarrow SiH^+ + H$	
$H_2^*(v'' \geq 2) + S^+ \rightarrow SH^+ + H$	

Permitted Reverse Reactions and Charge Transfer

$CH^+ + H \rightarrow C^+ + H_2(v''=0)$
$MgH^+ H \rightarrow Mg^+ + H_2(v''=0 \rightarrow 5)$
$SiH^+ + H \rightarrow Si^+ + H_2(v''=0, 1, 2)$
$SH^+ + H \rightarrow S^+ + H_2(v''=0, 1)$
$H^+ + OH \rightarrow H + OH^+$
$H^+ + CH \rightarrow H + CH^+$
$C^+ + CH \rightarrow C + CH^+$
$H + CO^+ \rightarrow H^+ + CO$

Secondary Reactions

Ions with neutral molecules	Atoms with molecular ions
$C^+ + OH \rightarrow CO^+ + H$	$O + CH^+ \rightarrow CO^+ + H$
$C^+ + OH \rightarrow CO + H^+$	$O + CH^+ \rightarrow CO + H$
$C^+ + CH \rightarrow C_2^+ + H$	$O + SiH^+ \rightarrow SiO^+ + H$
$C^+ + CH \rightarrow C_2 + H^+$	$N + CH^+ \rightarrow CN^+ + H$
$C^+ + NH \rightarrow CN^+ + H$	$N + CH^+ \rightarrow CN + H^+$
$C^+ + NH \rightarrow CN + H^+$	$N + SiH^+ \rightarrow SiN^+ + H$
$Si^+ + OH \rightarrow SiO^+ + H$	$N + SH^+ \rightarrow NS^+ + H$
$Si^+ + CH \rightarrow SiC^+ + H$	$N + OH^+ \rightarrow NO + H$
$Si^+ + NH \rightarrow SiN^+ + H$	$N + OH^+ \rightarrow NO^+ + H$
$S^+ + CH \rightarrow SC^+ + H$	$O + OH^+ \rightarrow O_2 + H^+$
$S^+ + CH \rightarrow SC + H^+$	$O + OH^+ \rightarrow O_2^+ + H$
$S^+ + NH \rightarrow SN^+ + H$	$O + MgH^+ \rightarrow MgO^+ + H$

TABLE III

A List of "Absentee" Molecules

SiH	MgC^+	SiS
SH	MgC	$MgSi^+$
SiC	MgN^+	MgSi
SiN	MgN	MgS^+
SN	SO^+	MgS
SiO	SO	
MgO	SiS^+	

The molecules in the left hand column may be formed by recombination of electrons from ions which are present (see text).

TABLE IV

Photodissociation Rates, ζ, in Units of $10^{-9} s^{-1}$ for the Radiation Field Described in the Text, and Allowance for Extinction

Molecule	ζ
CH	2.2
C_2	0.8
SC	2.9
NO	3.9
O_2	0.8

TABLE V

Photodissociation Rates Adopted for the Radiation Field Described in the Text, with Allowance for Extinction. "Fast" implies a rate of $10^{-8}s^{-1}$, and "slow" a rate of $10^{-9}s^{-1}$.

Fast		Slow	
OH	SN^+	CH^+	CN
CH	NO	OH^+	SiO^+
NH	NO^+	CO^+	SiC^+
SiH^+	O_2	CO	SiN^+
SH^+	O_2^+	C_2^+	MgO^+
SC^+	NH^+	C_2	
SC	MgH^+	CN^+	

TABLE VI

Number densities in cm^{-3} of Various Molecules Calculated for our Model of the ζ Oph Cloud, with $n(H_2) = 10^2 cm^{-3}$

Neutrals		Ions			
OH	5×10^{-5}	CH^+	8×10^{-6}	SiN^+	1.5×10^{-9}
CH	2×10^{-6}	SiH^+	3×10^{-7}	SC^+	4×10^{-10}
NH	2×10^{-6}	SH^+	6×10^{-8}	SN^+	5×10^{-10}
CO	1.5×10^{-6}	OH^+	3×10^{-7}	NO^+	3×10^{-10}
C_2	10^{-7}	CO^+	8×10^{-8}	O_2^+	1.5×10^{-8}
CN	6×10^{-7}	C_2^+	10^{-8}	MgH^+	10^{-7}
SC	8×10^{-10}	CN^+	4×10^{-8}	MgO^+	10^{-9}
NO	5×10^{-10}	SiO^+	3×10^{-8}		
O_2	5×10^{-9}	SiC^+	10^{-9}		

TABLE VII

A Comparison Between Observed and Calculated Column Densities in the Direction of ζ Oph. The CO Observation is from Smith and Stecher (1971), the Other Observations from Herbig (1968). The Calculations Refer to the Model Described in the Text, with $n(H_2) = 10^2 cm^{-3}$. The Column Densities are in Units of cm^{-2}.

Molecule	Observation	Calculation
CO	1.8×10^{15}	6×10^{13}
CN	8.7×10^{12}	10^{12}
CH^+	2.6×10^{13}	3×10^{13}
CH	4.3×10^{13}	0.8×10^{13}
NH	$<7.4 \times 10^{12}$	8×10^{12}
OH	$<8.3 \times 10^{13}$	2×10^{14}
MgH	$<4.3 \times 10^{12}$	0
SiH	$<5.6 \times 10^{12}$	0
CO^+	$<3.5 \times 10^{13}$	3×10^{11}