

## ASSOCIATIVE IONIZATION PROCESSES WITHIN INTERSTELLAR CLOUDS

SIMON PETRIE<sup>1</sup> AND DIETHARD K. BOHMEDepartment of Chemistry and Centre for Research in Earth and Space Science, York University,  
North York, Ontario, Canada M3J 1P3

Received 1993 December 27; accepted 1994 May 18

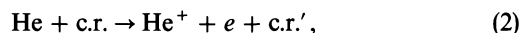
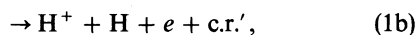
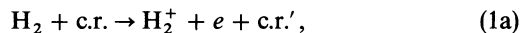
## ABSTRACT

Several exothermic associative ionization (AI) processes involving atoms or diatomic radicals are considered as sources of molecular ions and neutrals within diffuse and dense interstellar clouds. Most of the exothermic AI reactions identified are of the form  $M + O \rightarrow MO^+ + e$ , where  $M$  is a transition or rare-earth metal atom. Of those transition metals for which the AI reaction  $M + O$  is calculated to be exothermic, Ti has the largest cosmic abundance by more than one order of magnitude. However, the associative ionization of  $Ti + O$  may well be endothermic, in which case IS abundances of the ions  $ScO^+$  and  $ZrO^+$  (formed in significantly exothermic AI reactions) may exceed that of  $TiO^+$ . An examination of the energetics governing formation and loss processes for  $MO^+$  and  $MO$  suggests that scandium- and zirconium-containing  $MO$  and  $MO^+$  are likely to be more reliable indicators of IS transition metal depletion than are species containing titanium, and search strategies reflecting this possibility are recommended. Prospects for the detection of  $ZrO$  or  $ZrO^+$ , especially, are substantially enhanced by the comparative paucity of loss processes for these species. Since many other metal monoxide ions are expected to be removed effectively by reaction with atomic carbon, prospects for their detection in O-rich environments appear significantly better than in C-rich regions.

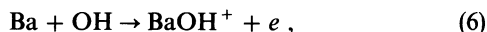
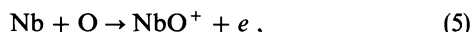
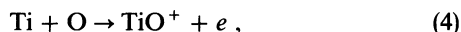
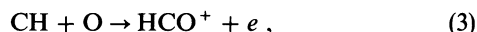
*Subject headings:* atomic processes — molecular processes

## 1. INTRODUCTION

The apparent connection between ionization and the formation of simple (largely organic) molecules within diffuse and dense interstellar (IS) clouds has long been appreciated (Watson 1974). It follows that sources of ionization within IS environments are therefore sources of chemical complexity, and several such sources can be considered. The dominant ionization mechanism in dense IS clouds is held to be cosmic-ray ionization

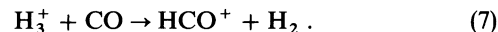


since these clouds are opaque to UV irradiation. However, within dense clouds the flux of energetic cosmic rays is substantially reduced from the typical flux encountered in more diffuse regions. Dalgarno and coworkers (Dalgarno, Oppenheimer, & Berry 1973; Oppenheimer & Dalgarno 1977) have identified several possible associative ionization (AI) reactions,

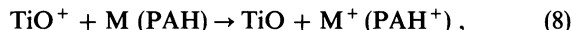


which can act as sources of molecular ions and of free electrons in IS clouds. Of the product ions,  $HCO^+$  has been reported widely within dense IS clouds but can be generated by a multitude of other processes under IS conditions, most notably by

the proton-transfer reaction



Nevertheless, Millar & Williams (1975) have suggested that reaction (3) is the most efficient pathway to  $HCO^+$  within dense IS clouds. Searches for interstellar  $TiO$ , which would result from neutralization of  $TiO^+$ ,



have to date proved negative (Churchwell et al. 1980); a search for  $TiO^+$  has not yet been performed. Other recent surveys concerned, in part, with titanium interstellar chemistry (Millar et al. 1987; Turner 1991) have attributed the apparent absence of interstellar  $TiO$  in several environments to the endothermicity of reaction (4); recent laboratory reevaluations of transition metal ion bond strengths (Fisher et al. 1990; Clemmer et al. 1991) suggest that reaction (4) is exothermic, albeit thermoneutral within experimental uncertainty. The possible exothermicity of reaction (4) and the exothermicity of other reactions such as (5) have two important implications. First, experimental studies of AI (Weiner, Masnou-Seeuws, & Giusti-Suzor 1990; Cockett et al. 1991a) suggest that such processes are usually efficient when exothermic and should therefore occur even at the very low temperatures ( $T \approx 10$ – $100$  K) of dense IS clouds. Second, the dissociative recombination process



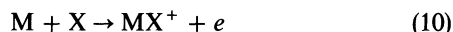
must be endothermic if reaction (4) is exothermic, and so this method of neutralization (highly efficient for most molecular ions) will not serve to deplete interstellar  $TiO^+$  which should, in consequence, have a very long lifetime.

In this work, we investigate the possible IS significance of several other AI reactions which are considered to be exothermic according to recent laboratory data.

<sup>1</sup> Present address: Department of Chemistry, University College, U.N.S.W., Australian Defence Force Academy, Canberra, ACT 2600, Australia.

## 2. THERMOCHEMISTRY OF ASSOCIATIVE IONIZATION

The exothermicity of a generalized AI reaction



can be expressed as  $-\Delta H_{10} = D(M^+ - X) - IE(M)$ , where  $D(M^+ - X)$  is the strength of the chemical bond formed and  $IE(M)$  is the ionization energy of the more easily ionized reactant  $M$ . Chemical bond formation does not generally provide sufficient energy to ionize an atom or small radical or molecule, and so this criterion is met infrequently for ground-state reactants. A reaction of type (10) is most likely to be exothermic if one reactant  $M$  has a low ionization energy, and if the other reactant  $X$  is capable of forming a strong bond (ideally, a double or triple bond) with  $M^+$ . Reactants that can satisfy this requirement are, as  $M$ , various metals (notably transition and rare-earth metals) and, as  $X$ , the strongly electronegative elements oxygen, fluorine, and chlorine; oxygen, having a greater tendency to form multiple bonds, appears the best candidate among these species. Nitrogen also has a tendency to form double or triple bonds, but is less electronegative than oxygen:

it appears that bonds between transition metal ions and N are generally somewhat weaker than  $M^+ - O$  bonds (Kunze & Harrison 1989). Several exothermic reactions of type (10) can be identified from current thermochemical information (Lias et al. 1988; Martinho Simoes & Beauchamp 1990); these reactions are listed in Table 1.

It might be argued that the list of possible AI reactions given in Table 1 reflects something of a current experimental bias—that is, thermochemical quantities exist that permit the calculation of a substantially greater number of  $M^+ - O$  bond strengths than is currently possible for  $M^+ - F$ ,  $M^+ - N$ , or  $M^+ - Cl$  bonds. While this criticism is, in a sense, valid, it appears unlikely that further experimental values will alter the current predominance of O-atom reactions as viable interstellar AI processes, since such comparisons of  $M^+ - X$  bond strengths as are currently possible indicate that these bonds are generally strongest for  $X = O$ . Thus, it is highly probable that  $M + O$  reactions do account for the most common class of exothermic AI reactions. Furthermore, the abundance of O in IS environments is much greater than that of F, N, or Cl. In the discussion that follows, we shall therefore consider specifically

TABLE 1

EXOTHERMIC OR NEAR-THERMONEUTRAL ASSOCIATIVE IONIZATION PROCESSES OF POSSIBLE INTERSTELLAR SIGNIFICANCE

Reactants <sup>a</sup>	$IE(M)^b$	$D(M^+ - X)^c$	$-\Delta H^d$	$IE(MX)^e$	$T_c(M)^f$	$n(M)^g$
CH + O .....	10.64 ± 0.01	10.84 ± 0.06	0.20 ± 0.07	8.10 ± 0.05	...	...
Sc + O .....	6.562 ± 0.005 <sup>h</sup>	7.14 ± 0.11 <sup>i</sup>	0.60 ± 0.12	6.43 ± 0.16 <sup>i</sup>	1664	1100
Ti + O <sup>j</sup> .....	6.820 ± 0.006 <sup>h</sup>	6.88 ± 0.07 <sup>i,k</sup>	0.06 ± 0.08	6.819 ± 0.006 <sup>l</sup>	1549	87200
Y + O .....	(6.22)	(7.80)	(1.58)	5.85 ± 0.15	1592	150
Zr + O <sup>j</sup> .....	6.84 ± 0.05	9.04 ± 0.3	2.20 ± 0.35	(6.1 ± 0.3)	≈ 1780	475
Nb + O .....	6.88 ± 0.05	(9.0 ± 2.3)	(2.1 ± 2.4)	(6.1 ± 0.5)	≈ 1550	44
La + O <sup>m</sup> .....	5.577 ± 0.005	8.98 ± 0.1	3.40 ± 0.1	4.90 ± 0.1	1520	14
Ce + O <sup>m</sup> .....	5.5387 ± 0.0004	8.99 ± 0.1	3.45 ± 0.1	4.90 ± 0.1	1500	37
Pr + O <sup>n</sup> .....	5.464 ± 0.006	8.30 ± 0.1	2.76 ± 0.1	4.90 ± 0.1	1532	4.7
Nd + O <sup>n</sup> .....	5.5250 ± 0.0006	7.84 ± 0.1	2.31 ± 0.1	4.97 ± 0.1	1510	25
Sm + O <sup>n</sup> .....	5.6437 ± 0.0006	6.03 ± 0.1	0.39 ± 0.1	5.55 ± 0.1	1515	7.1
Gd + O <sup>j,n</sup> .....	6.1502 ± 0.0006	7.82 ± 0.1	1.67 ± 0.1	5.75 ± 0.1	1545	9.3
Tb + O .....	5.8639 ± 0.0006	7.60 ± 0.1	1.74 ± 0.1	5.62 ± 0.1	1560	1.73
Dy + O .....	5.9390 ± 0.0006	6.22 ± 0.1	0.28 ± 0.1	6.08 ± 0.1	1571	11.3
Ho + O .....	6.0216 ± 0.0006	6.19 ± 0.1	0.17 ± 0.1	6.17 ± 0.1	1568	2.5
Er + O .....	6.2077 ± 0.0006	6.11 ± 0.1	0.0 ± 0.1	6.30 ± 0.1	1590	7.1
Lu + O .....	5.4259 ± 0.0001	5.81 ± 0.1	0.38 ± 0.1	6.79 ± 0.1	1597	1.1
Hf + O .....	6.78 ± 0.05	7.54 ± 0.1	0.76 ± 0.15	7.55 ± 0.1	1652	4.7
Ta + O .....	7.40 ± 0.05	8.17 ± 0.1	0.77 ± 0.15	7.92 ± 0.1	≈ 1550	0.66
Y + F .....	(6.22)	6.15 ± 0.1	(-0.07)	6.3 ± 0.3	1592	150
Sr + F .....	5.695 ± 0.005	6.26 ± 0.3	0.57 ± 0.3	5.0 ± 0.3	...	846
Ba + F .....	5.212 ± 0.005	6.41 ± 0.3	1.2 ± 0.3	4.8 ± 0.3	...	150
Y + Se .....	(6.22)	(9.0 ± 1)	(2.8 ± 1)	6.1 ± 1	1592	150
Ba + OH <sup>j,n</sup> .....	5.212 ± 0.005	5.52 ± 0.1	0.41 ± 0.1	4.35 ± 0.3	...	150

<sup>a</sup> Neutral reactants, in their ground states.

<sup>b</sup> Ionization energy (in eV) of the "metal" or more easily ionized reactant, obtained from the tabulation of Lias et al. 1988 unless otherwise specified.

<sup>c</sup> Bond dissociation energy (in eV) of the ion  $MX^+$ , calculated (using the "ion convention") from 298 K thermochemical values obtained from the tabulation of Lias et al. 1988 unless otherwise specified. In those instances where  $MX^+$  is not a diatomic ion, the bond energy specified is that for the bond formed in the associative ionization reaction.

<sup>d</sup> Exothermicity of associative ionization (in eV), calculated as  $D(M^+ - X) - IE(M)$ .

<sup>e</sup> Ionization energy (in eV), obtained from the tabulation of Lias et al. 1988 unless otherwise specified.

<sup>f</sup> 50% condensation temperature (in K, at  $10^{-4}$  atm) for the more refractory reactant species, obtained from Wasson 1985. Absent values indicate a value lower than 400 K.

<sup>g</sup> Cosmic abundance of the "metal"  $M$ , expressed relative to  $n(H) = 1 \times 10^{12}$ , obtained from the meteoritic abundances tabulated by Trimble 1975.

<sup>h</sup> Ionization energy obtained from Sugar & Corliss 1985.

<sup>i</sup> Value obtained from Clemmer et al. 1991.

<sup>j</sup> This reaction has been studied experimentally by Lo & Fite 1974.

<sup>k</sup> A value of  $6.93 \pm 0.10$  eV has been given by Fisher et al. 1990.

<sup>l</sup> Value obtained from Sappéy et al. 1989.

<sup>m</sup> This reaction has been studied experimentally by Cockett et al. 1991a.

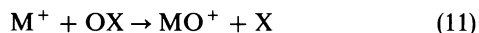
<sup>n</sup> This reaction has been studied experimentally by Cockett et al. 1991b.

the formation of oxygen-containing diatomic ions  $MO^+$  by associative ionization.

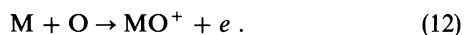
### 3. REACTIONS INVOLVED IN PRODUCTION AND REMOVAL OF $MO^+$ IONS

A mechanism for the formation and reaction of  $MO^+$  and related species is given in Table 2. Many of the reactions listed here have been considered in earlier discussions of IS titanium chemistry (Openheimer & Dalgarno 1977; Churchwell et al. 1980; Millar et al. 1987) and also have a bearing on the IS chemistry of other transition metals. In the present context, some of the reactions listed in Table 2 require further comment.

Millar et al. (1987) have commented that reaction (11),



with  $O_2$  or  $H_2O$ , will dominate by one or two orders of magnitude over the AI reaction (12) in the dense-cloud production of  $TiO^+$ :



Examples of reaction (11) have been measured—for example, the reactions of  $Sc^+$ ,  $Ti^+$ , and  $Zr^+$  with  $O_2$  (Dheandhanoo, Chatterjee, & Johnsen 1985; Fisher et al. 1990)—do occur at close to the collision rate when exothermic. Reactions of type (11) are also likely to be a major dense-cloud source of  $MO^+$  for metals other than titanium and are not necessarily limited to those metals  $M$  for which the AI reaction (12) is exothermic:

TABLE 2

MECHANISM FOR PRODUCTION AND REACTION OF THE SPECIES  $MO^+$ ,  $MO$ ,  $M^+$ , AND  $M$  IN DIFFUSE OR DENSE IS CLOUDS

Reaction	Rate Coefficients Used <sup>a</sup>
$M + O \rightarrow MO^+ + e$	$10^{-11}$
$M + A^+ \rightarrow M^+ + A$	$10^{-9}$
$M + hv \rightarrow M^+ + e$	$10^{-10}$
$M^+ + B^c \rightarrow M + B^+$	$10^{-9}$
$M^+ + e \rightarrow M + hv$	$10^{-11}$
$M^+ + PAH^- \rightarrow M + PAH$	$10^{-7}$
$M^+ + OX^d \rightarrow MO^+ + X$	$10^{-9}$
$MO + E^+ \rightarrow MO^+ + E$	$10^{-8}$
$MO + G^+ \rightarrow M^+ + O + G$	$10^{-8}$
$MO + hv \rightarrow MO^+ + e$	$10^{-10}$
$MO + C \rightarrow M + CO$	$10^{-10}$
$MO^+ + J^g \rightarrow MO + J^+$	$10^{-9}$
$MO^+ + e \rightarrow MO + hv$	$10^{-11}$
$MO^+ + PAH^- \rightarrow MO + PAH$	$10^{-7}$
$MO^+ + hv \rightarrow M^+ + O$	$10^{-10}$
$MO^+ + C \rightarrow M^+ + CO$	$10^{-9}$

<sup>a</sup> All reaction rate coefficients and recombination coefficients are expressed in units of  $cm^3 \text{ molecule}^{-1} s^{-1}$ .

<sup>b</sup>  $A^+$  is any species for which charge transfer to  $M$  is efficient. As a simplification, we assume that charge transfer is rapid when exothermic:  $IE(A) > IE(M)$ . Examples:  $He^+$ ,  $H^+$ .

<sup>c</sup>  $B$  is any species for which charge transfer from  $M^+$  is efficient. As a simplification, we assume that charge transfer is rapid when exothermic:  $IE(B) < IE(M)$ . Examples:  $Na$ ,  $K$ .

<sup>d</sup>  $OX$  is any oxygen-containing species for which the bond strength  $D(O-X) < D(M^+-O)$ . Examples:  $OH$ ,  $O_2$ .

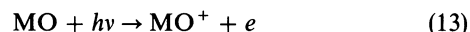
<sup>e</sup>  $E^+$  is any species for which charge transfer (but not dissociative charge transfer) to  $MO$  is exothermic:  $IE(MO) < IE(E) < IE(MO) + D(M^+-O)$ . Examples:  $NO^+$ ,  $OH^+$ .

<sup>f</sup>  $G^+$  is any species for which dissociative charge transfer to  $MO$  is exothermic:  $IE(G) > IE(MO) + D(M^+-O)$ . Examples:  $He^+$ ,  $H^+$ .

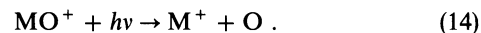
<sup>g</sup>  $J$  is any species for which charge transfer from  $MO^+$  is exothermic:  $IE(J) < IE(MO)$ . Examples:  $Na$ ,  $K$ .

however, it should be noted that if reaction (12) is endothermic, then the reverse process of dissociative recombination will be exothermic and presumably very efficient. We note also that there exist some metal ions— $Ce^+$ ,  $La^+$ ,  $Zr^+$ , and probably  $Nb^+$ —for which reaction (11) involving  $CO$  is exothermic. Given the very high abundance for  $CO$  within dense clouds, formation rates for the ions  $CeO^+$ ,  $LaO^+$ ,  $NbO^+$ , and  $ZrO^+$  are likely to be substantially larger than for other  $MO^+$  involving metals of comparable IS abundance, for which reaction (11) with  $CO$  is endothermic.

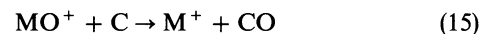
Treatment of photodissociation and photoionization processes is problematic given the large differences in UV attenuation for diffuse and dense clouds. We also make the simplifying assumption here that photodissociation of  $MO$  is negligible in any event, since photoionization according to reaction (13)



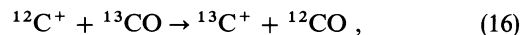
requires less energy and is expected to be efficient for photons of sufficient energy. Photodestruction of the  $MO$  bond is effected only through dissociation of  $MO^+$ , reaction (14):



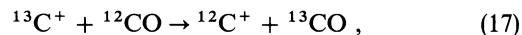
Destruction of  $MO^+$  by reaction (15)



with atomic carbon has not been considered in any previous models, but appears in many instances to offer the major route to  $MO^+$  removal. The abundance of  $C$  in diffuse and dense clouds is generally large (Phillips & Huggins 1981; Jaffe et al. 1985; Keene et al. 1985). Reaction (15) is exothermic for those  $MO^+$  species having a bond strength  $D(M^+-O) < D(C\equiv O)$  (8.57 eV). Evidence that the oxygen-abstraction reaction (15) will probably be efficient when exothermic is offered by the near-thermoneutral isotope-exchange reactions



and



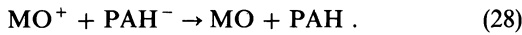
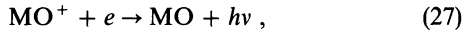
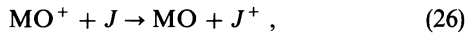
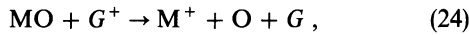
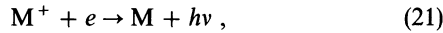
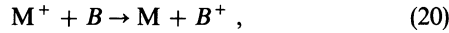
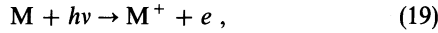
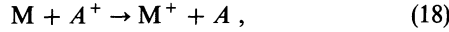
for which rate coefficients of  $k_{16} = 4.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$  and  $k_{17} = 6.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$  have been determined at 80 K using a SIFT apparatus (Smith & Adams 1980). The rate coefficients for these reactions are very close to the values expected upon statistical grounds for an essentially thermoneutral reaction lacking any activation energy barriers, and we can assume by comparison that reaction (15), in those instances that involve exothermic cleavage of a bond of less strength than the  $C\equiv O$  bond, will occur at the collision rate ( $k \approx 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ ). We note that reaction (15) is endothermic for  $ZrO^+$ ,  $LaO^+$ ,  $CeO^+$ , and probably  $NbO^+$ , and therefore the IS removal rates for these ions are expected to be somewhat lower than for other  $MO^+$ .

Precise measurements of IS abundances and depletions, for most of the metal atoms considered as reactants in Table 1, are unavailable at present. However, since many of the metals considered have similar condensation temperatures ( $T_c \approx 1500 \text{ K}$ ) (Wasson 1985), most of these species should have broadly similar depletions within a "typical" diffuse cloud. The situation with respect to dense cloud metal atom abundances is more problematic, since accretion of metal atoms onto dust grains is expected to account for substantial additional depletion of these elements in the gas phase under such conditions.

Nevertheless, we consider (as a first approximation) that all of the metal atoms  $M$  for which reaction (12) is exothermic will be depleted similarly within a given dense cloud.

#### 4. MODELING OF $MO/MO^+$ FORMATION AND DESTRUCTION

The mechanism for gas-phase  $M/M^+$  chemistry given in Table 2 can be used to estimate abundance ratios for the species  $M/M^+/MO/MO^+$ , if it is assumed that a dynamic equilibrium is attained between these species under IS cloud conditions. Reactions of type (11) to (15) and (18) to (28) have been included in the model.



Rate coefficients used in the calculations of reaction rates and examples of each type of reaction are given in Table 2.

Equilibrium abundance ratios for  $M^+$ ,  $MO$ , and  $MO^+$  relative to  $M$  can be expressed:

$$M^+ : M = \frac{k_{18}[A^+] + k_{19}I_{UV} + ([MO]/[M])k_{24}[G^+] + ([MO^+]/[M])(k_{14}I_{UV} + k_{15}[C])}{k_{20}[B] + \alpha_{21}[e] + k_{22}[PAH^-] + k_{11}[OX]}, \quad (29)$$

$$MO : M = \frac{([MO^+]/[M])(k_{26}[J] + \alpha_{27}[e] + k_{28}[PAH^-])}{k_{23}[E^+] + k_{24}[G^+] + k_{13}I_{UV} + k_{25}[C]}, \quad (30)$$

$$MO^+ : M = \frac{k_{12}[O] + ([M^+]/[M])k_{11}[OX] + ([MO]/[M])(k_{23}[E^+] + k_{13}I_{UV})}{k_{26}[J] + \alpha_{27}[e] + k_{28}[PAH^-] + k_{14}I_{UV} + k_{15}[C]}. \quad (31)$$

Expressions (29) to (31) have been solved iteratively, using the assumed reactant abundances given in Table 3. The overall mechanism adopted is somewhat simplistic and is intended to be representative of transition metal chemistry in IS clouds, but may very well not be comprehensive in its treatment of metal atom reactivity. Furthermore, it should be noted that very significant variations exist, for the abundances of several of the key reactants in Table 3, between individual clouds in either the "diffuse" or "dense" category. For example, several groups (Liszt 1985; Liszt & Vanden Bout 1985; Goldsmith & Young 1989; Combes et al. 1991) have documented substantial differences in the fractional abundance of  $O_2$  within various sources. Such variations, which presumably reflect variations

TABLE 3  
ADOPTED MODEL ABUNDANCES OF REACTANT SPECIES

Reactant <sup>a</sup>	$n_{diff}^b$	$n_{dense}^c$	Comments
O	$10^{-4}$	$10^{-5}$	...
$A^+$	$10^{-5}$	$10^{-8}$	...
$hv$	0.5	0	...
B	$10^{-7}$	$2 \times 10^{-7}$	Ce, Dy, La, Lu, Nd, Pr, Sm, Tb
	$5 \times 10^{-7}$	$4 \times 10^{-7}$	Er, HO
	$10^{-6}$	$5 \times 10^{-7}$	Gd, Hf, Nb, Sc, Ti, Y, Zr
	$5 \times 10^{-6}$	$10^{-6}$	Ta
e	$10^{-4}$	$10^{-7}$	...
$PAH^-$	$10^{-9}$	$10^{-8}$	...
OX	$10^{-6}$	$10^{-5}$	...
$CO^d$	$10^{-5}$	$10^{-4}$	...
$E^+$	$10^{-5}$	$10^{-8}$	...
$G^+$	$10^{-7}$	$10^{-9}$	...
C	$10^{-4}$	$10^{-5}$	...
J	$10^{-8}$	$10^{-8}$	Ce, La, Pr, Nd
	$10^{-7}$	$2 \times 10^{-7}$	Gd, Sm, Tb, Y
	$5 \times 10^{-7}$	$4 \times 10^{-7}$	Dy, Nb, Zr
	$10^{-6}$	$5 \times 10^{-7}$	Er, Hf, Ho, Lu, Sc, Ti
	$5 \times 10^{-6}$	$10^{-6}$	Ta

<sup>a</sup> Reactant species as given in mechanism detailed in Table 2.

<sup>b</sup> Abundance of reactant X, expressed relative to hydrogen,  $n(X)/n(H + 2H_2)$ , for reactant species in "typical" diffused cloud.

<sup>c</sup> Abundance of reactant X, expressed relative to hydrogen,  $n(X)/n(H + 2H_2)$ , for reactant species in "typical" dense cloud.

<sup>d</sup> For Ce, La, Nb, and Zr, CO also reacts as OX (see text).

in the  $O/O_2$  ratio will therefore influence the relative significance of reactions (11) and (12) within individual clouds. A consideration of all such effects, and of the time dependence of reactant or product abundances, is beyond the scope of the present model: we hope merely to attain an indication of the general prospects for  $M-O$  bond formation under IS conditions, with particular emphasis on some important reactivity differences between different metals  $M$ .

Results of these model calculations, for diffuse and dense cloud conditions, respectively, are given in Tables 4 and 5. Several different sets of conditions have been employed, as indicated in these tables, to determine the influence of particular reactions upon the calculated abundances. General findings are as follows.

Under diffuse cloud conditions:

1. Ions ( $M^+$ ,  $MO^+$ ) predominate over neutrals ( $M$ ,  $MO$ ), due to photoionization and charge-transfer reactions: thus the  $M^+ : MO^+$  ratio serves to characterize the relative efficiency of  $M-O$  bond formation and bond destruction processes.

2. The photodissociation of  $MO^+$  is the predominant process of  $M-O$  bond destruction. Variation of the UV flux causes a near-identical degree of variation in the  $M^+ : MO^+$  ratio under the range of conditions modeled. Therefore, prospects for detection of  $M-O$  containing species are better within clouds having a greater degree of UV attenuation.

3. Associative ionization is a minor source of  $MO^+$ —variation of the AI reaction rate coefficient  $k_{12}$ , from zero to  $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , has negligible impact upon the  $M^+ : MO^+$  ratio. The major source of  $MO^+$  is, therefore, the reaction of  $M^+$  with O-containing radicals and molecules (principally OH). More generally, because of the predominance of ionized M-containing species, neutral chemistry is of little consequence. Variation of the reaction rate coefficient  $k_{12}$  and/or  $k_{25}$  has very little effect on the abundances of the various metallic species.



TABLE 4  
RESULTS OF MODEL CALCULATIONS FOR DIFFUSE CLOUD CONDITIONS

Model	Metal	M <sup>a</sup>	M <sup>+</sup> <sup>a</sup>	MO <sup>a</sup>	MO <sup>+</sup> <sup>a</sup>
1. "Standard" model <sup>b</sup> .....	Most <sup>c</sup>	0.03	0.96	$7 \times 10^{-5}$	$7 \times 10^{-3}$
	Ce, La, Nb, Zr	0.03	0.80	$2 \times 10^{-3}$	0.17
	Ta	0.09	0.90	$3 \times 10^{-4}$	$7 \times 10^{-3}$
2. "Low UV" <sup>d</sup> .....	Gd, Hf, Sc, Ti, Y	0.12	0.87	$1 \times 10^{-4}$	0.01
	Dy, Lu, Nd, Pr, Sm, Tb	0.07	0.92	$1 \times 10^{-4}$	0.01
	Ce, La, Nb, Zr	0.04	0.30	$7 \times 10^{-3}$	0.65
	Ho, Er	0.09	0.90	$2 \times 10^{-4}$	0.01
	Ta	0.27	0.72	$5 \times 10^{-4}$	0.01
3. "High UV" <sup>e</sup> .....	Most <sup>c</sup>	$3 \times 10^{-4}$	0.99	$4 \times 10^{-6}$	$2 \times 10^{-3}$
	Ce, La, Nb, Zr	$3 \times 10^{-3}$	0.98	$4 \times 10^{-5}$	0.02
	Ta	0.01	0.99	$2 \times 10^{-5}$	$2 \times 10^{-3}$
4. "MO + C off" <sup>f</sup> .....	Most <sup>c</sup>	0.03	0.96	$7 \times 10^{-5}$	$7 \times 10^{-3}$
	Ce, La, Nb, Zr	0.03	0.79	$2 \times 10^{-3}$	0.18
	Ta	0.09	0.90	$3 \times 10^{-4}$	$7 \times 10^{-3}$
5. "M + O fast" <sup>g</sup> .....	Most <sup>c</sup>	0.02	0.97	$7 \times 10^{-5}$	$8 \times 10^{-3}$
	Ce, La, Nb, Zr	0.02	0.80	$2 \times 10^{-3}$	0.18
	Ta	0.08	0.91	$4 \times 10^{-4}$	0.01
6. "M + O off" <sup>h</sup> .....	Most <sup>c</sup>	0.03	0.96	$6 \times 10^{-5}$	$6 \times 10^{-3}$
	Ce, La, Nb, Zr	0.03	0.80	$1 \times 10^{-3}$	0.17
	Ta	0.09	0.90	$2 \times 10^{-4}$	$6 \times 10^{-3}$
7. "X <sup>+</sup> + MO fast" <sup>i</sup> .....	Most <sup>c</sup>	0.03	0.96	$1 \times 10^{-5}$	$7 \times 10^{-3}$
	Ce, La, Nb, Zr	0.03	0.79	$2 \times 10^{-4}$	0.18
	Ta	0.09	0.90	$4 \times 10^{-5}$	$7 \times 10^{-3}$
8. "X <sup>+</sup> + MO, M + O fast" <sup>j</sup> .....	Most <sup>c</sup>	0.03	0.96	$1 \times 10^{-5}$	$8 \times 10^{-3}$
	Ce, La, Nb, Zr	0.02	0.80	$2 \times 10^{-4}$	0.18
	Ta	0.08	0.91	$6 \times 10^{-5}$	0.01
9. "Neutral reaction off" <sup>k</sup> .....	Most <sup>c</sup>	0.03	0.96	$7 \times 10^{-5}$	$6 \times 10^{-3}$
	Ce, La, Nb, Zr	0.03	0.80	$2 \times 10^{-3}$	0.17
	Ta	0.09	0.90	$2 \times 10^{-4}$	$6 \times 10^{-3}$
10. "M + O endothermic" <sup>l</sup> .....	Ti	0.05	0.95	$6 \times 10^{-7}$	$9 \times 10^{-5}$
	Ho, Er	0.04	0.96	$8 \times 10^{-7}$	$9 \times 10^{-5}$

<sup>a</sup> Abundance of indicated transition-metal species, expressed as a fraction of the total gas-phase abundance of species containing the indicated metal M.

<sup>b</sup> All reaction rate coefficients and conditions as specified in Tables 2 and 3, respectively.

<sup>c</sup> Dy, Er, Gd, Hf, Ho, Lu, Nd, Pr, Sc, Sm, Tb, Ti, Y.

<sup>d</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $n(h\nu)/n(\text{H} + 2\text{H}_2) = 0.05$ .

<sup>e</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $n(h\nu)/n(\text{H} + 2\text{H}_2) = 5$ .

<sup>f</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{25} = 0$ .

<sup>g</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = 10^{-10}$ .

<sup>h</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = 0$ .

<sup>i</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{23} = k_{24} = 10^{-7}$ .

<sup>j</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{23} = k_{24} = 10^{-7}$  and  $k_{12} = 10^{-10}$ .

<sup>k</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = k_{25} = 0$ .

<sup>l</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = 0$  and with reaction (30) modified:  $\text{MO}^+ + e \rightarrow \text{O}, k_{30} = 10^{-7}$ .

4. AI is also of low significance as an ionization process within diffuse clouds. The total degree of ionization of M-containing species does not change significantly with variation in  $k_{12}$ .

Under dense cloud conditions:

1. Reactions with atomic carbon are the predominant processes for M—O bond destruction. For Zr, Nb, La, and Ce, reaction (25) is the principal destruction process; for the other metals studied, reactions (15) and (25) are of comparable significance in bond destruction.

2. Neutrals (M, MO) dominate over ions (M<sup>+</sup>, MO<sup>+</sup>), although the ratio M:M<sup>+</sup> is significantly larger than MO:MO<sup>+</sup> under most assumed conditions. The associative ionization reaction (12) is a significant contributor to the degree of ionization of M-containing species: the ratio

(M<sup>+</sup> + MO<sup>+</sup>):(M + MO) is near unity if reaction (12) is fast, and is negligible if reaction (12) is prohibitively slow. Reaction (12) is also the principal source of M—O bond formation for most of the metals included in this model.

Several effects are common to both cloud types:

1. Abundances of MO and MO<sup>+</sup> are substantially higher relative to the abundances of the equivalent atomic species M and M<sup>+</sup> for the metals Ce, La, Nb, and Zr than for the other metals included in the model. The phenomenon arises, as suggested earlier, as a result of the wider range of neutrals (including CO) for which oxygen-abstraction reaction (11) is possible, and the endothermicity of reaction (15), for Ce, La, Nb, and Zr.

2. Lower M<sup>+</sup>:M and MO<sup>+</sup>:MO ratios are systematically seen for Ta than for the other metals included in the model,

TABLE 5  
RESULTS OF MODEL CALCULATIONS FOR DENSE CLOUD CONDITIONS

Model	Metal	M <sup>a</sup>	M <sup>+</sup> <sup>a</sup>	MO <sup>a</sup>	MO <sup>+</sup> <sup>a</sup>
1. "Standard" model <sup>b</sup> .....	Most <sup>c</sup>	0.87	0.04	0.05	0.04
	Ce, La, Nb, Zr	0.82	$8 \times 10^{-5}$	0.09	0.09
	Ta	0.90	0.02	0.05	0.03
2. "MO + C off" <sup>d</sup> .....	Most <sup>c</sup>	0.48	0.03	0.45	0.04
	Ce, La, Nb, Zr	0.04	$8 \times 10^{-5}$	0.88	0.08
	Ta	0.45	0.02	0.50	0.03
3. "M + O fast" <sup>e</sup> .....	Most <sup>c</sup>	0.44	0.16	0.22	0.18
	Ce, La, Nb, Zr	0.34	$6 \times 10^{-5}$	0.34	0.32
	Ta	0.49	0.12	0.25	0.14
4. "M + O off" <sup>f</sup> .....	Most <sup>c</sup>	0.99	$4 \times 10^{-3}$	$4 \times 10^{-3}$	$3 \times 10^{-3}$
	Ce, La, Nb, Zr	0.98	$9 \times 10^{-5}$	0.01	$9 \times 10^{-3}$
5. "X <sup>+</sup> + MO fast" <sup>g</sup> .....	Most <sup>c</sup>	0.87	0.05	0.03	0.05
	Ce, La, Nb, Zr	0.77	$1 \times 10^{-4}$	0.08	0.15
	Ta	0.90	0.03	0.03	0.04
6. "X <sup>+</sup> + MO, M + O fast" <sup>h</sup> .....	Most <sup>c</sup>	0.42	0.20	0.15	0.23
	Ce, La, Nb, Zr	0.27	$3 \times 10^{-4}$	0.26	0.47
	Ta	0.48	0.16	0.18	0.18
7. "Neutral reactions off" <sup>i</sup> .....	Most <sup>c</sup>	0.91	$6 \times 10^{-3}$	0.08	$5 \times 10^{-3}$
	Ce, La, Nb, Zr	0.34	$8 \times 10^{-5}$	0.60	0.06
	Ta	0.91	$4 \times 10^{-3}$	0.08	$4 \times 10^{-3}$
8. "M + O endothermic" <sup>j</sup> .....	Ti, Ho, Er	0.99	$1 \times 10^{-3}$	$9 \times 10^{-4}$	$7 \times 10^{-4}$

<sup>a</sup> Abundance of indicated transition-metal species, expressed as a fraction of the total gas-phase abundance of species containing the indicated metal M.

<sup>b</sup> All reaction rates coefficients and conditions as specified in Tables 2 and 3, respectively.

<sup>c</sup> Dy, Er, Gd, Ho, Lu, Nd, Pr, Sc, Sm, Tb, Ti, Y.

<sup>d</sup> Rate coefficients conditions as specified in Tables 2 and 3, except  $k_{25} = 0$ .

<sup>e</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = 10^{-10}$ .

<sup>f</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = 0$ .

<sup>g</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{23} = k_{24} = 10^{-7}$ .

<sup>h</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{23} = k_{24} = 10^{-7}$  and  $k_{12} = 10^{-10}$ .

<sup>i</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = k_{25} = 0$ .

<sup>j</sup> Rate coefficients and conditions as specified in Tables 2 and 3, except  $k_{12} = 0$  and with reaction (27) modified:  $\text{MO}^+ + e \rightarrow \text{M} + \text{O}$ ,  $k_{27} = 10^{-7}$ .

due to the comparatively high ionization energies of Ta and TaO. Removal of these ions by charge transfer occurs with higher efficiency than it does for the other ions modeled.

3. Reactions of M or M<sup>+</sup> with atomic oxygen or with O-containing species produce MO or MO<sup>+</sup>, while reactions with atomic carbon serve to deplete MO and MO<sup>+</sup>. This suggests that detection of MO or MO<sup>+</sup> is more probable within oxygen-rich than within carbon-rich IS environments.

## 5. DISCUSSION

The model adopted in the previous sections reveal several significant points. The proportion of (neutral and ionized) metal monoxides to the corresponding gas-phase metal atoms is expected to be larger within dense clouds than within diffuse clouds, so dense clouds appear a more promising site for detection of M—O-containing species. However, transition metal depletion within dense clouds is generally more severe than in diffuse clouds: thus detection of metal monoxides, especially those of metals which have a low cosmic abundance, may be problematic within either environment. Species whose detection appears most favored are TiO, ScO, ZrO, NbO, LaO, CeO, and their positive ions. Detection of TiO is favored by the large cosmic abundance of Ti; however, as noted earlier, there is uncertainty in the thermochemistry of several key reactions involving Ti, and TiO<sup>+</sup> formation by reaction (12) may not be viable while destruction of TiO<sup>+</sup> by electron recombi-

nation may be very efficient. Dissociative recombination of TiO<sup>+</sup> (if efficient) would be of particular importance in diffuse cloud chemistry, since the fractional abundance of free electrons is much higher in diffuse than in dense clouds. TiO is the only metal monoxide considered here that has yet been sought within IS clouds and has not been detected (Churchwell et al. 1980; Millar et al. 1987). Experimental evidence, which may support the proposal that reaction (12) featuring Ti is endothermic (or inhibited by an activation energy barrier), is that the cross section for this reaction at  $\approx 2000$  K is approximately 1/20th of that observed for the corresponding reaction of Zr or of Gd under the same conditions (Lo & Fite 1974).

Scandium is the next most abundant of the transition metals featured in Table 1, so a search for ScO or ScO<sup>+</sup> may be worthwhile. Detection of ScO or ScO<sup>+</sup> in the absence of the corresponding Ti-containing species would also suggest strongly (if it is assumed that depletions of Sc and Ti within an IS cloud are comparable) that reaction (12) for Ti is endothermic or inhibited in some manner: reaction (12) for Sc is substantially exothermic. The other metals whose monoxides may be detectable are of lower cosmic abundance, and presumably will be as depleted under IS conditions as are Ti and Sc: however, the production of CeO, LaO, NbO, and their positive ions is favored by several factors, as we have noted. Of these species, Zr has the largest cosmic abundance by about a factor of 10, so a search for ZrO or ZrO<sup>+</sup> appears more likely to

TABLE 6  
EXPECTED ISOTOPE ABUNDANCES AND SPECTRAL FEATURE  
DISTRIBUTIONS FOR MO OR MO<sup>+</sup> (M = Sc, Ti, Zr)

MO	Percent Natural Abundance <sup>a</sup>	$\mu(\text{MO})^b$	$f_i^c$
<sup>45</sup> ScO .....	100%	$4.13 \pm 0.21^d$	$f_b$
<sup>46</sup> TiO .....	8.0	$2.96 \pm 0.05^e$	$1.010862 \times f_b$
<sup>47</sup> TiO .....	7.3		$1.005307 \times f_b$
<sup>48</sup> TiO .....	73.8		$f_b$
<sup>49</sup> TiO .....	5.5		$0.994890 \times f_b$
<sup>50</sup> TiO .....	5.4		$0.989999 \times f_b$
<sup>90</sup> ZrO .....	51.45	$2.551 \pm 0.011^f$	$f_b$
<sup>91</sup> ZrO .....	11.27		$0.998337 \times f_b$
<sup>92</sup> ZrO .....	17.17		$0.996713 \times f_b$
<sup>94</sup> ZrO .....	17.33		$0.993564 \times f_b$
<sup>96</sup> ZrO .....	2.78		$0.990546 \times f_b$

<sup>a</sup> Natural terrestrial isotope abundance, obtained from the compilation of Heath 1986.

<sup>b</sup> Experimental dipole moment of ground-state MO, in debye.

<sup>c</sup> Characteristic frequency of the isotopic species identified, expressed as a multiple of the base frequency  $f_b$  for the most abundant isotope.

<sup>d</sup> Rice & Field 1986.

<sup>e</sup> Steimle & Shirley 1989.

<sup>f</sup> Suenram et al. 1990.

succeed than a search for the monoxides of Ce, La, and Nb. Interstellar identification of ZrO (whose microwave spectrum has been investigated by Suenram et al. 1990) or of ZrO<sup>+</sup> may be facilitated by the existence of four reasonably abundant isotopes, which would help to confirm the identity of any spectral feature attributed to these species. Terrestrial isotope abundances for Sc, Ti, and Zr are used in Table 6 to predict the distribution of spectral features expected for the monoxides of these metals.

The destruction of MO and MO<sup>+</sup> by reactions with atomic carbon is less efficient for M = Ce, La, Nb, or Zr than it is for the other transition metal species considered here. In this regard, comparisons of M:MO or M:MO<sup>+</sup> within IS clouds, for, say, M = Sc and M = Zr, could provide a diagnostic for the C/O ratio within these clouds, since ScO and ScO<sup>+</sup> should be more efficiently scavenged by atomic carbon than should ZrO and ZrO<sup>+</sup>. Furthermore, since species having low ioniza-

tion energy are almost entirely ionized within diffuse clouds, the endothermicity of reaction (15) for M = Ce, La, Nb, and Zr is particularly significant in diffuse cloud chemistry, and a very large enhancement in ZrO<sup>+</sup>:Zr<sup>+</sup> (relative to, say, the ratio ScO<sup>+</sup>:Sc<sup>+</sup>) is anticipated within such clouds.

## 6. CONCLUSIONS

Several associative ionization processes, which have not previously been considered in the context of IS cloud chemistry, do appear to be viable as sources of metal monoxide (MO) neutrals and ions within diffuse and dense IS clouds. The apparent absence of interstellar TiO may indicate that the AI reaction of Ti + O is inefficient under IS conditions (presumably because of its endothermicity). An interstellar search for the species ScO, ZrO, and their positive ions may indicate whether the absence of TiO is due to the endothermicity of AI in this instance or, rather, reflects a severe depletion of transition metal atoms in the IS sources in which TiO has not been detected.

AI reactions of IS significance almost always involve reactions of atomic oxygen with a metal atom, most usually an "early" transition metal or a rare-earth metal (these elements being characterized by very high M<sup>+</sup>-O bond strengths). While reactions of metal atoms with other species (notably OH, F, and Se) may also lead to AI, few such examples can currently be identified, and these other reactants generally have much lower IS abundances than those expected for atomic oxygen.

Metal monoxide ions MO<sup>+</sup> formed by AI reactions are likely to be most effectively destroyed by oxygen-abstraction reactions with atomic carbon—although this route will not serve to deplete ZrO<sup>+</sup>, LaO<sup>+</sup>, CeO<sup>+</sup>, or probably NbO<sup>+</sup>. Other metal monoxide ions are expected to have substantially higher abundances in O-rich environments than in C-rich regions, and so searches for these ions (and the corresponding neutrals) should focus on oxygen-rich IS clouds and circumstellar shells.

D. K. B. thanks the Natural Sciences and Engineering Research Council of Canada for the financial support of this research and the Canada Council for a Killam Research Fellowship.

## REFERENCES

- Churchwell, E., Hocking, W. H., Merer, A. J., & Gerry, M. C. L. 1980, *AJ*, 85, 1382
- Clemmer, D. E., Ekind, J. L., Aristov, N., & Armentrout, P. B. 1991, *J. Chem. Phys.*, 95, 3387
- Cockett, M. C. R., Dyke, J. M., Ellis, A. M., & Wright, T. G. 1991a, *J. Chem. Soc. Faraday Trans.*, 87, 19
- Cockett, M. C. R., Nyulási, L., Veszprémi, T., Wright, T. G., & Dyke, J. M. 1991b, *J. Electron Spectrosc. Relat. Phenom.* 57, 373
- Combes, F., Casoli, F., Encrenaz, P. J., Gerin, M., & Laurent, C. 1991, *A&A*, 248, 607
- Dalgarno, A., Oppenheimer, M., & Berry, R. S. 1973, *ApJ*, 183, L21
- Dheandhanoo, S., Chatterjee, B. K., & Johnsen, R. 1985, *J. Chem. Phys.*, 83, 3327
- Fisher, E. R., Ekind, J. L., Clemmer, D. E., Georgiadis, R., Loh, S. K., Aristov, N., Sunderlin, L. S., & Armentrout, P. B. 1990, *J. Chem. Phys.*, 93, 2676
- Goldsmith, P. T., & Young, J. S. 1989, *ApJ*, 341, 718
- Heath, R. L. 1986, in *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast et al. (67th ed.; Boca Raton, FL: CRC Press), B-219
- Jaffe, D. T., Harris, A. I., Silber, M., Genzel, R., & Betz, A. L. 1985, *ApJ*, 290, L59
- Keene, J., Blake, G. A., Phillips, T. G., Huggins, P. J., & Beichman, C. A. 1985, *ApJ*, 299, 967
- Kunze, K. L., & Harrison, J. F. 1989, *J. Phys. Chem.*, 93, 2983
- Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D., & Mallard, W. G. 1988, *J. Phys. Chem. Ref. Data*, 17, Suppl. 1
- Liszt, H. S. 1985, *ApJ*, 298, 281
- Liszt, H. S., & Vanden Bout, P. A. 1985, *ApJ*, 291, 178
- Lo, H. H., & Fite, W. L. 1974, *Chem. Phys. Lett.*, 29, 39
- Martinho Simoes, J. A., & Beauchamp, J. L. 1990, *Chem. Rev.*, 90, 629
- Millar, T. J., Eildér, J., Hjalmarsen, Å., & Olofsson, H. 1987, *A&A*, 182, 143
- Millar, T. J., & Williams, D. A. 1975, *MNRAS*, 170, 51P
- Oppenheimer, M., & Dalgarno, A. 1977, *ApJ*, 212, 683
- Phillips, T. G., & Huggins, P. J. 1981, *ApJ*, 251, 533
- Rice, S. F., & Field, R. W. 1986, *J. Molec. Spectrosc.*, 119, 331
- Sappay, A. R., Eiden, G., Harrington, J. E., & Weisshaar, J. C. 1989, *J. Chem. Phys.*, 90, 1415
- Smith, D., & Adams, N. G. 1980, *ApJ*, 242, 424
- Steimle, T. C., & Shirley, J. E. 1989, *J. Chem. Phys.*, 91, 8000
- Suenram, R. D., Lovas, F. J., Fraser, G. T., & Matsumura, K. 1990, *J. Chem. Phys.*, 92, 4724
- Sugar, J., & Corliss, C. 1985, *J. Phys. Chem. Ref. Data*, 14, Suppl. 2
- Trimble, V. 1975, *Rev. Mod. Phys.*, 47, 877
- Turner, B. E. 1991, *ApJ*, 376, 573
- Wasson, J. T. 1985, *Meteorites: Their Record of Early Solar-System History* (New York: Freeman)
- Watson, W. D. 1974, *ApJ*, 188, 35
- Weiner, J., Masnou-Seeuws, F., & Giusti-Suzor, A. 1990, *Adv. Atom. Molec. Phys.*, 26, 209