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Radiative Association Reactions of Na^+, Mg^+, and Al^+ with Abundant Interstellar Molecules. Variational Transition State Theory Calculations

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Ab initio calculations using G2 theory and other methods have been performed for the collision complexes of the metal ions Na^+, Mg^+, and Al^+ with the molecules H_2, CO, N_2, NH_3, H_2O, HCN, HNC, C_2H_2, C_2H_4, c−C_3H_2, H_2CCC, H_2CCCC, and HCCCN. Binding energies, vibrational frequencies, and infrared intensities obtained from these calculations have been used to perform variational transition state theory (VTST) calculations for the corresponding radiative association reactions at temperatures pertinent to dense interstellar clouds and the outer regions of circumstellar envelopes. The calculated rate coefficients for radiative association reactions with H_2 and with the other smaller molecules of this group are slow compared with the chemical evolutionary time scale of cold interstellar clouds. For the largest and most strongly bound complexes considered, the rate of depletion of M^+ by this mechanism becomes competitive with recombination of M^+ with free electrons. Predicted rates for association in several systems at high pressure are in order-of-magnitude agreement with experiments, except for Mg^+/H_2O, which is predicted to be substantially faster than a recent experimental upper limit.

Introduction

In sharp contrast to the chemistry of the cosmically abundant nonmetallic elements H, C, N, O, Si, and S in dense interstellar clouds, the gas-phase chemical evolution of the abundant metals Na, Mg, Al, K, Ca, Ti, Fe, and Ni within such objects has received very little attention. Several factors have contributed to this lack of study. First, it is generally assumed that the metal atoms within interstellar clouds must be largely accreted onto dust-grain surfaces, and that therefore their contribution to the gas-phase chemical processing of a typical cloud is fairly minor. Second, the conventional wisdom has been that interstellar cloud chemistry is dominated by ion/molecule chemistry, and that the interstellar chemistry of metal ions is restricted to two main classes of reaction: charge-transfer reactions with neutrals (few of which have ionization energies low enough to permit charge transfer) and (slow) radiative recombination with free electrons. Third, the experimental study of gas-phase reactions of metal-containing species is seldom straightforward, particularly under conditions capable of yielding results applicable to the low temperatures of interstellar clouds; metals are generally very refractory, and isolation of internally cold, ground-state metal-containing ions or neutrals within the gas phase can be very difficult. Early studies, which involved the reactions of Na^+ [1] and Mg^+ [2] with some small molecules of high interstellar abundance, indicated that these ions reacted only sparingly (and solely by association) with the neutrals in question.

More recently, the assumed "minor role" for gas-phase metals within interstellar clouds has been questioned. Again, there are several factors to which this revision of our understanding can be attributed. First, and most obviously, the observation of various metal-containing molecules (to date, NaCl, AlF, AlCl, KCl, Na(CN), MgCN, and MgNC) within the envelope of the carbon-rich, mass-losing star IRC +10216[3−7] suggests that gas-phase metal atoms or ions are capable of molecule formation under interstellar or circumstellar conditions. Most of these species [all of the metal halides and Na(CN)] are localized within the hot inner envelope of IRC +10216,[8] and presumably are formed by processes of thermochemical equilibrium under conditions that are very different from those found within dense interstellar clouds; but MgNC at least (and almost certainly MgCN also) is more abundant within the cold outer envelope than within the warmer inner regions,[9] indicating that it probably arises by pathways[10] that are also accessible within dense interstellar clouds. Second, an experimental study[11] of the reactions of Fe^+ with small unsaturated hydrocarbons (several of which are expected to be abundant within interstellar clouds) has found that most of these reactions exhibit termolecular association (at a temperature of 300 K and a helium bath gas pressure of 0.35 Torr) with an efficiency that is a significant fraction of the collision rate for these systems. It has been argued that the radiative association of Fe^+ with unsaturated hydrocarbons, and with other abundant interstellar "nucleophiles" such as HCN, HCCCN, NH_3, and c−C_3H_2, is also likely to be efficient at low temperatures.[11] Several recent studies[12−19] have also suggested a significant role for metal ions, and transition metal ions in particular, in reactions with interstellar polycyclic aromatic hydrocarbons. It has been argued, for example, that the rich chemistry of metal ions with hydrocarbons may have implications for the formation of polycyclic aromatic hydrocarbons (PAHs),[18] for the reduction of interstellar oxygen

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TABLE 1: Total Energies, Enthalpies of Formation, and Ion/Ligand Binding Energies for Metal-Containing Molecular Ions MX^+

		M = Na		M = Mg			M = Al	
X	$E_0(X)^a$	$E_0(NaX^+)^a$	$MCA(X)^b$	$\langle s^2\rangle^c$	$E_0(MgX^+)^a$	$MCA(X)^b$	$E_0(AlX^+)^a$	$MCA(X)^b$
H_2	−1.16636	−162.83415	9.4^d	0.75	−200.53188	5.8^d	−242.88064	3.6^d
CO	−113.17749	−274.85297^{e,f}	43.1^f	0.75	−312.55825	43.8	−354.90228	30.8
N_2	−109.39261	−271.06473^{e,f}	34.2^f	0.76	−308.76928	33.0	−351.113330	20.2
H_2O	−76.33205	−238.02765^{e,f}	95.9^f	0.75	−275.74426	126.4	−318.08664	109.1
NH_3	−56.45865	−218.15942^{e,f}	109.5^f	0.75	−255.88154	154.4	−298.22471	139.2
HCN	−93.28489	−254.98417^e	105.5^e	0.75	−292.69980	133.4^g		121.8^h
HNC	−93.26199	−254.96128^e	105.6^e	0.75	−292.67622	131.4^g		121.8^h
C_2H_2	−77.18574	−238.86645^e	56.8^e	0.75	−276.577414	72.4	−318.920156	56.1
C_2H_4	−78.41593	−240.09693^e	57.6^e	0.75	−277.80803	73.6	−320.150540	56.6
$c-C_3H_2$	−115.14028	−276.85453^i	147.1^{i,j}	0.75	−314.58268	205.6	−356.92526	188.9
H_2CCC	−115.11958	−276.83030^i	135.4^{i,j}	0.94	−314.56789	221.2	−356.89650	167.7
H_2CCCC			142.0^k	1.34		149.4^k		175.9^k
HCCCN^l	−169.29597	−331.00256	111.1	0.78	−368.71318	139.5	−411.05986	131.5

[a] Total energy, in Hartrees, including ZPE. Unless otherwise indicated, this parameter is at the G2 level of theory. [b] Calculated metal cation affinity (MCA), in kJ mol^{-1}, of the ligand X. [c] Spin expectation value (0.75 for pure doublet), at the MP2(full)/6-31G* level. [d] G2(QCI(thaw)) value, obtained according to the method described in ref 41. [e] G2(thaw) value, obtained according to the method described in ref 41. [f] Previously reported.[41] [g] Previously reported.[51] [h] Previously reported.[53] [i] G2(MP2(thaw/MP2)) value, calculated according to the method described in ref 41. [j] Previously reported.[52] [k] Calculated as the quantity $E_e(M^+) + E_e(X) - E_e(MX^+)$ at the QCISD(T)/6-311G**//MP2(full)/6-31G* level of theory. [l] Values reported for this species are for the G2(MP2) level of theory.

molecules,[13] and for the speciation of iron within the diffuse interstellar medium.[17] Even at room temperature the radiative association of metal ions with aromatic hydrocarbons[15,20−23] and with other macrocyclic compounds[24,25] is often fast, and such reactions are expected to be almost universally efficient at interstellar cloud temperatures.

The occurrence of association reactions of the abundant metal ions with interstellar molecules[26] may have important implications for cloud chemical evolution, even if these reactions do not lead to significant abundances of any metal-containing molecules. The dissociative recombination of metal-containing molecular ions MX^+

$$MX^+ + e \rightarrow M + X \tag{1}$$

is expected to be more efficient by several orders of magnitude than the radiative recombination of atomic metal ions

$$M^+ + e \rightarrow M + h\nu \tag{2}$$

Conversion of M^+ to MX^+ by radiative association thus provides a pathway by which ionized metals can be neutralized efficiently; it also provides a means of limiting the abundance of free electrons within dense clouds. Most models of cloud chemical evolution are constructed with the assumption that the gas-phase metal abundances are very low, because appreciable abundances of unreactive Na^+, Mg^+, or Fe^+ would imply also an abundance of free electrons that is too high to permit significant chemical evolution of H, C, N, O, and S via ion/molecule reactions.[27,28] If the main reservoirs of ionized metals are as molecular ion adducts rather than as atomic ions, however, a high gas-phase metal abundance can be sustained without the production of a prohibitively large free-electron abundance, because of the high rate coefficient expected for reactions of type (**1**). Given the limitations of the present knowledge of metal speciation within interstellar environments, it is not possible to determine whether gas-phase metal abundances are low or high; but it is not correct to assume, as has been done traditionally, that these abundances are necessarily low.

One important, increasingly powerful method of chemical investigation is via computation, and in recent years it has become possible to obtain highly accurate binding energies (see, for example, refs 29, 30) and vibrational frequencies[31] of small molecules, radicals, and ions, by the implementation of ab initio quantum chemical procedures. Such methods are invaluable for investigating the structures of collision complexes that may be difficult to study via experiment. Recent work has combined such quantum-chemical molecular information with transition-state theory kinetic methods to calculate accurate and reliable radiative association (RA) reaction rate coefficients.[20−22,32−36]

Theoretical Methods

The structural, thermochemical, and spectroscopic parameters required for computation of RA rate coefficients were obtained by ab initio calculations; in all instances, these were performed using the GAUSSIAN94 programming suite.[37] For most species, metal/ligand bond strengths were determined using the Gaussian-2 (G2) or G2(MP2) theoretical procedures[38,39]: these techniques generally are regarded to be reliable to within ±10 kJ mol^{-1}.[29] For the sodium ion adducts, the calculated bond strengths from standard G2 theory may be somewhat low because of shortcomings inherent in the frozen-core approximation used in G2,[38,40,41] and several values were used, as indicated in Table 1, from recent corrected calculations. For adducts of the metal ions with H_2, calculations were performed at the QCISD(T)/6-311+G(3df,2p)//QCISD(full)/6-311G** level of theory, with the correlation space for this QCISD(T) single-point calculation defined to include all filled orbitals except the 1s orbital on Na, Mg, or Al. Fundamental vibrational frequencies, in most cases, were obtained at the HF/6-31G* and MP2/6-31G* levels of theory, and corrected by scale factors of 0.8929 and 0.9427, respectively; zero-point vibrational frequencies were found using the same technique, albeit with the application of different scale factors.[31] Dipole moments, quadrupole moments, and polarizabilities of the neutral molecules were calculated using the HF/6-31G*, MP2(full)/6-31G*, and B3-LYP/6-31G* levels of theory.

The RA process is pictured as a two-step sequence, in which a metastable complex ML^{+*} is formed by collision, after which it either redissociates to reactants or stabilizes by emission of an IR photon.

$$M^+ + L \rightleftharpoons ML^{+*} \rightarrow ML^+ + h\nu \tag{3}$$

The overall kinetics of this process is characterized by a bimolecular rate constant k_{ra}. The association/dissociation aspects of the kinetics can be treated by transition-state theory (TST).[42] The following expression[32,42] gives the correct canonical association rate constant within two assumptions: (1) the global assumptions of TST (notably the assumption of no isolated regions of phase space, and the approximation of no recrossings of the optimized transition-state dividing surface); and (2) the assumption that a single photon emission, or a single collision with a neutral molecule, relaxes the metastable ML^{+*} complex sufficiently so that its stabilization is assured (the "sudden-death" assumption):

$$k_2 = \frac{1}{hQ_{\mathrm{reactants}}} \int\int \mathrm{d}E\mathrm{d}J\, N_{EJ}\, e^{-E/kT} \times \left\{ \frac{k_{\mathrm{r}}(E,J) + k_{\mathrm{c}}(E,J)[M]}{k_{\mathrm{b}}(E,J) + k_{\mathrm{r}}(E,J) + k_{\mathrm{c}}(E,J)[M]} \right\} \quad (4)$$

where k_2 is the effective bimolecular association rate constant, $Q_{\mathrm{reactants}}$ is the canonical partition function of the separated reactants, N_{EJ} is the number-of-states function of the transition state, $k_{\mathrm{r}}(E,J)$ is the photon emission rate constant of the complex, k_{c} is the stabilization rate constant for collisions with bath gas at concentration $[M]$, $k_{\mathrm{b}}(E,J)$ is the redissociation rate constant of the metastable complex, and E and J are the total energy and total angular momentum of the system. The radiative association rate coefficient k_{ra} is the low-pressure limit of k_2 (i.e., the limit at which k_{c} is negligibly small).

Most accurately, this approach can be implemented using the framework of variational transition state theory (VTST).[32] In the limit of low association efficiency a simpler approach becomes useful, because the properties of the transition state drop out of the calculation. Then the calculation approaches the "thermal" theory developed by Bates and Herbst.[43] The photon emission rate is a weak function of the internal energy and angular momentum of the metastable complex, and the appropriate convolution over energy and angular momentum is incorporated in the present calculations. For the few cases in the present study where the association efficiency is not low (that is, where $k_{\mathrm{ra}} \geq 10^{-12}$), full VTST methods were used. (Bates and Herbst developed an empirically justified "modified thermal model" for approximating such cases and applied it with some success,[43] but the present full VTST calculation is suggested as being based more soundly on rigorous VTST theory, and not difficult to implement in practice.) The potential function used included the isotropic ion-induced dipole potential and the ion−dipole potential. Trials showed that other potential terms, such as the anisotropic polarizability contributions to the ion-induced dipole potential, and the ion-quadrupole potential, were completely insignificant in these systems. Vibrational adiabaticity of the conserved modes was assumed in the VTST treatment.

The sudden-death assumption made here is strongly justifiable in treating RA in the present systems. The justification for its application to the collisional association cases treated briefly below is less clear-cut, both because of the poor energy-transfer capacity of He bath gas, and also because of the much higher temperature. The estimates discussed below for collisional association at room temperature, although they seem to be in reasonable order-of-magnitude agreement with experiment, are thus not really satisfactory. Avoiding this approximation, detailed master equation treatments of ion−neutral association kinetics have been reported; see for instance ref 44 and the references cited therein. Future high-pressure theoretical work on the present systems will need to address these questions.

For nonpolar neutrals in the long-range potential of the ion−neutral interaction, the VTST approach is equivalent to phase-space theory (PST),[45−48] but for the strongly polar neutrals of interest here, VTST is different from, and more accurate than, simple PST. It is thus a more appropriate approach for cases outside the low-efficiency limit.

TABLE 2: Calculated Parameters for the Neutrals X, Obtained at the MP2(full)/6-31G* Level of Theory

X	μ^a	Q^b			α^c		
		xx	*yy*	*zz*	*xx*	*yy*	*zz*
H_2	0	2.0393	2.0393	1.6175	0	0	0.926
CO	0.4376	9.9748	9.9748	12.1051	1.177	1.177	1.962
N_2	0	10.3658	10.3658	11.7270	0.914	0.914	1.924
H_2O	2.2436	7.2501	4.1333	5.9679	0.420	1.046	0.774
NH_3	1.9684	6.1079	6.1079	8.8848	1.371	1.371	0.820
HCN	3.2539	11.7509	11.7509	9.4501	1.124	1.124	2.850
HNC	2.7350	11.7972	11.7972	9.7813	1.308	1.308	2.959
C_2H_2	0	13.4783	13.4783	6.4377	1.127	1.127	3.937
C_2H_4	0	15.4836	12.2446	11.9824	1.212	2.971	4.284
c-C_3H_2	3.3457	17.3761	14.1200	21.6115	1.975	4.478	3.887
H_2CCC	4.0650	17.7572	17.7118	19.5799	2.058	2.700	7.513
H_2CCCC	4.2765	25.2189	21.3388	26.0285	2.360	3.222	12.490
HCCCN	4.2477	22.8638	22.8638	20.3590	1.970	1.970	8.862

[a] Dipole moment, in Debye. [b] Quadrupole moment, in Debye Ångstroms. [c] Polarizability, in Å^3.

The other major component governing the kinetics is the emission rate k_{r} of IR photons, and a principal feature of the present calculations is the computation of rates using a reasonably satisfactory level of ab initio theory. The theoretical framework for deriving k_{r} from ab initio values of the frequencies and IR intensities of the vibrational modes of the ML^+ complex has been described in detail.[22,36,49]

Finally, the RA kinetics are a strong function of the binding energy of the ML^+ complex. These binding energies are known for a few ion/neutral pairs of interstellar interest and generally must be calculated. A principal focus of the present work is the calculation at the G2 level or higher of binding energies for several cases.

The kinetics calculations were performed using the VariFlex program suite,[50] which gives convenient unified implementation of the procedures outlined above. The low-temperature calculations of H_2 assumed pure *para*-hydrogen and conservation of the nuclear spin in the complex, although use of normal hydrogen statistics would not make a very large difference. The rotational levels of H_2 and the MH_2^+ complexes were summed explicitly, whereas the other calculations used the high-temperature approximation to rotational statistics.

Results and Discussion

The ab initio quantum chemical data of relevance to this study are presented in Tables 1 to 4. In several instances, most notably for sodium-containing ions, the equilibrium geometries, total energies, and other parameters obtained using G2 theory have been reported previously[10,40,51−53]; most of the magnesium- and aluminum-containing ions have not been studied previously at this level of theory. Various experimental and theoretical studies of these complexes have been reported. Some recent values of binding energies are shown in Table 5.

Total energies and metal cation affinities are given in Table 1. Structural parameters for the neutrals X and molecular ions MX^+, necessary for the calculation of RA rate coefficients, are shown in Tables 2 and 3, respectively. Comparison of the calculated molecular parameters with reported values[54] indicates that our dipole moments of polar species generally are accurate to within ± 0.5 D, but are overestimated more often than underestimated; whereas the calculated polarizabilities are often

TABLE 3: Calculated Rotational Parameters for the Molecular Ions MX^+, Obtained at the MP2(full)/6-31G* Level of Theory

		M = Na			M = Mg			M = Al		
X	$\sigma(MX^+)$[a]	A[b]	B[b]	C[b]	A[b]	B[b]	C[b]	A[b]	B[b]	C[b]
H_2	2	1824.62	43.94	42.91	1832.49	22.42	22.15	1834.98	20.63	20.40
CO	1		3.549			3.660			2.958	
N_2	1		3.994			3.915			3.021	
H_2O	2	422.70	9.457	9.457	409.27	10.68	10.41	402.47	10.09	9.847
NH_3	3	190.65	8.435	8.435	188.62	9.617	9.617	186.86	9.213	9.213
HCN	1			4.251			4.558		4.097	
HNC	1			3.773			4.002		3.566	
C_2H_2	2	34.52	5.983	5.099	34.36	6.439	5.423	34.42	5.369	4.645
C_2H_4	2	24.60	5.411	4.722	24.44	5.706	4.940	24.53	4.663	4.140
c-C_3H_2	2	31.70	2.979	2.723	31.42	3.222	2.922	31.37	3.017	2.753
H_2CCC	2	290.00	2.001	1.987	288.55	2.430	2.410	288.67	1.957	1.943
H_2CCCC	2	285.76	1.207	1.202	291.22[c]	1.380[c]	1.374[c]	285.03	1.168	1.163
HCCCN	1		1.304			1.374			1.267	

[a] Rotational symmetry number of the ion MX^+. [b] Rotational constant of MX^+, in GHz. When only B is shown, the equilibrium geometry of MX^+ is linear. [c] From calculations at the B3-LYP/6-31G* level of theory.

too low by a factor of 2. The errors manifested in our calculated rate coefficients arising from any inaccuracies in these parameters are not expected to outweigh errors caused by inaccurate binding energy determinations: k_{ra} is more sensitive to the binding energy than to the parameters in Table 2. In fact, the dependence on the Table 2 parameters tends to vanish for most of the reactions treated here that proceed with low efficiency. Moreover, for the polar species, any errors in low-temperature rate coefficient values arising from inaccuracies in the dipole moments and in the polarizabilities are expected to cancel each other in large part.

Finally, the vibrational frequencies associated with each MX^+ species are tabulated in Table 4. Calculations of structural parameters and vibrational frequencies were also undertaken at other levels of theory − HF/6-31G* for ion structures and frequencies, and HF/6-31G* and B3-LYP/6-31G* for neutral polarizabilities and dipole and quadrupole moments. Except where specified further, the agreement between different levels of theory was good.

Some general trends are apparent in these results. First, the metal ion/ligand bond energies are generally lowest for Na^+ (with polar neutrals) or Al^+ (with nonpolar neutrals) and highest for Mg^+, although the relationship is not systematic; the most glaring exception to this trend is in the M^+/H_2 bond energies, for which the relatively high $Na^+{-}H_2$ bond energy (assessed against those for Mg^+ and Al^+) is consistent with the relatively small ionic radius for sodium. Second, the relative metal ion/ligand bond energies (as a function of varying the ligands) fall in the sequence H_2 < (CO, N_2) < (HCCH, C_2H_4) < (H_2O, NH_3, HCN, HNC) < (c−C_3H_2, H_2CCC, H_2CCCC), reflecting the change from essentially pure van der Waals complexes (with H_2), through π- and σ-complexes, to partially covalent adducts of carbenes (C_3H_2 and H_2CCCC). The most weakly bound complexes involve the most abundant interstellar reactants (H_2 and CO), whereas the strongest metal−ligand interactions involve highly polar neutrals of typically fairly low interstellar abundance.

The calculated rate constants are given in Table 6. For each neutral and each metal ion, the k_{ra} values are tabulated for three temperatures: 10, 30, and 100 K. For each case a measure of the binding energy dependence ("slope") is also given, and the rate of emission of IR photons from the complex (where the complex has $J = 0$ and its internal energy is just equal to the binding energy with no additional thermal energy). The rates qualitatively follow the expected trend, in that the association rate increases rapidly with increasing size (degrees of freedom) of the system, with increasing binding energy, and with decreasing temperature. With the exception only of the largest and most strongly bound systems in this study, the association efficiencies are low (i.e., the rate constants are much less than the collision rate, which is about 10^{-9} cm^3 molec^{-1} s^{-1}).

Temperature Dependence. At low temperature with relatively small systems where the vibrational degrees of freedom of the reactants are frozen out, the thermal model of Bates and Herbst[43] gives the temperature dependence to an excellent approximation as $k_{ra} \propto T^{-(r+1)/2}$, where r is the sum of the rotational degrees of freedom of the reactants. This condition is well satisfied for all the present cases, and the thermal model prediction is expected to be valid at least for low-efficiency associations. As can be verified from the values given in Table 6, the present cases where $r = 2$ (linear) or 3 (nonlinear) have temperature dependences from 10 to 100 K that follow this expectation very well. Even for the cases where the low-efficiency approximation and the thermal model are not applicable (notably Mg^+/H_2CCC and Al^+/H_2CCCC) the temperature dependence still follows this expression to good accuracy.

Binding Energy Dependence. It has been observed that log k_{ra} is linearly proportional to the binding energy to a good approximation in various systems. This linear dependence was not tested systematically in this study, although sample checks indicated that this is a good representation of the form of the binding energy dependence for the present systems. Assuming this functional form, the strength of the dependence in a given system can be specified by giving the ratio of k_{ra} values calculated for two binding energy values differing by some specified amount. In Table 6, this is done by taking a binding energy increment of 10 kJ mol^{-1}, and reporting the ratio of rate constants corresponding to this increment. For almost all cases, the rate constant is approximately doubled when the binding energy increases by this amount.

Comparison with Reported Values. Table 5 compares the values used in the present work with various reported values. For Na^+ the recent completion of two careful, concordant experimental studies by different techniques[55,56] gives confidence that several sodium ion binding energies are now known well enough to anchor this scale. For Mg^+ and Al^+ the experimental situation is much less secure, although the experimental values from refs 57 and 58 are generally considered to be reliable anchors. Recent photofragmentation spectroscopy values for Mg^+/C_2H_4[59] and Al^+/C_2H_4[60] are also noteworthy. For those cases where recent experimental results are available, our values are mostly in agreement within an acceptable uncertainty of ∼10 kJ mol^{-1}. Our values are in good accord with other theoretical calculations at a similar or higher computational level.

TABLE 4: Fundamental Vibrational Frequencies, IR Emission Intensities, and Zero-Point Vibrational Energies for MX^+

X	M^+	ν_i[a] (I_i)[b]	[ZPE][c]
H_2	Na^+	274 (9.8), 429 (18), 4205 (20)	[11.459]
	Mg^+	65 (14), 117 (14), 4232 (18)	[10.303]
	Al^+	96 (6.4), 125 (13), 4242 (7.9)	[10.418]
CO	Na^+	170 (2.2)*, 179 (27), 2045 (3.5)	[5.984]
	Mg^+	180 (3.1)*, 197 (82), 2057 (0.65)	[6.101]
	Al^+	136 (85), 149 (0.055)*, 2038 (0.27)	[5.771]
N_2	Na^+	136 (3.9)*, 170 (30), 2070 (8.3)	[5.866]
	Mg^+	106 (0.13)*, 153 (91), 3520 (588)]	[9.070]
	Al^+	112 (67), 113 (0.72)*, 2054 (21)	[5.585]
H_2O	Na^+	304 (19), 333 (374), 430 (128), 1649 (119), 3545 (85), 3639 (178)	[23.113]
	Mg^+	336 (311), 387 (44), 505 (17), 1630 (149), 3486 (124), 3575 (237)	[23.158]
	Al^+	330 (97), 330 (360), 496 (25), 1613 (129), 3442 (160), 3541 (255)	[22.768]
NH_3	Na^+	298 (13), 485 (112)*, 1283 (168), 1646 (33)*, 3284 (15), 3402 (39)*	[37.194]
	Mg^+	381 (29), 572 (6.9)*, 1334 (203), 1627 (53)*, 3247 (36), 3360 (76)*	[37.539]
	Al^+	332 (74), 570 (8.7)*, 1342 (219), 1615 (63)*, 3222 (59), 3341 (82)*	[37.237]
HCN	Na^+	148 (60)*, 245 (30), 725 (36)*, 1981 (18), 3274 (128)	[16.916]
	Mg^+	148 (20)*, 301 (81), 760 (27)*, 2317 (440), 3301 (34)	[18.055]
	Al^+	132 (26)*, 227 (150), 736 (28)*, 1985 (78), 3253 (174)	[16.812]
HNC	Na^+	172 (50)*, 227 (25), 584 (160)*, 2001 (0.003), 3559 (389)	[17.040]
	Mg^+	187 (8.4)*, 283 (72), 614 (142)*, 2072 (2.6), 3524 (519)	[17.470]
	Al^+	152 (14)*, 221 (125), 603 (147)*, 2010 (17), 3524 (517)	[16.962]
C_2H_2	Na^+	166 (0.07), 203 (22), 452 (0.0), 536 (16), 716 (122), 769 (120), 1863 (9.2), 3224 (179), 3310 (4.5)	[26.238]
	Mg^+	230 (64), 235 (0.07), 458 (0.0), 585 (0.12), 721 (85), 803 (173), 1854 (32), 3199 (236), 3287 (14)	[26.551]
	Al^+	91 (2.8), 175 (90), 447 (0.0), 545 (1.9), 722 (95), 795 (180), 1860 (38), 3209 (211), 3297 (11)	[26.009]
C_2H_4	Na^+	124 (0.01), 189 (22), 211 (0.66), 807 (1.2), 942 (10), 991 (132), 1036 (0.0), 1195 (0.0), 1323 (5.6), 1430 (14), 1590 (6.1), 3013 (0.13), 3024 (0.53), 3098 (0.0), 3118 (0.10)	[51.575]
	Mg^+	213 (60), 261 (3.1), 301 (2.8), 808 (1.1), 994 (1.9), 1023 (192), 1036 (0.0), 1195 (0.0), 1320 (22), 1433 (23), 1576 (21), 3006 (7.1), 3016 (2.7), 3095 (0.0), 3113 (8.3)	[51.613]
	Al^+	42 (0.79), 168 (82), 253 (2.2), 807 (1.4), 944 (1.8), 1014 (199), 1029 (0.0), 1195 (0.0), 1324 (23), 1429 (13), 1586 (30), 3010 (2.6), 3022 (0.92), 3099 (0.0), 3116 (1.8)	[51.452]
c-C_3H_2	Na^+	140 (34), 202 (57), 233 (23), 771 (23), 907 (36), 921 (0.84), 943 (0.0), 1104 (25), 1317 (24), 1575 (3.6), 3136 (30), 3169 (9.2)	[33.663]
	Mg^+	158 (1.7), 209 (2.6), 301 (49), 778 (45), 913 (50), 937 (3.0), 940 (0.0), 1130 (21), 1322 (11), 1581 (16), 3135 (49), 3168 (19)	[34.023]
	Al^+	144 (0.90), 177 (2.7), 263 (100), 779 (47), 912 (64), 938 (4.6), 941 (0.0), 1130 (18), 1315 (2.7), 1576 (35), 3134 (54), 3167 (22)	[33.795]
H_2CCC	Na^+	108 (43), 109 (36), 240 (36), 305 (0.33), 344 (4.3), 1014 (1.2), 1048 (17), 1110 (31), 1443 (2.9), 2051 (300), 3006 (2.2), 3101 (7.5)	[32.403]
	Mg^+	46 (64), 119 (92), 418 (2.2), 427 (5.5), 507 (89), 693 (56), 1021 (0.27), 1086 (25), 1411 (0.27), 2171 (424), 3069 (18), 3177 (6.3)	[33.020]
	Al^+	69 (3.3), 84 (6.6), 252 (167), 254 (8.4), 281 (6.7), 1011 (0.23), 1065 (18), 1107 (177), 1436 (0.043), 2099 (258), 3009 (12), 3108 (19)	[32.163]
H_2CCCC	Na^+	81 (24), 83 (29), 236 (45), 264 (4.3), 271 (8.3), 479 (3.8), 541 (0.007), 783 (89), 895 (12), 895 (24), 1308 (17), 1717 (58), 2130 (739), 3000 (152), 3088 (48)	[36.818]
	Mg^+[d]	77 (60), 119 (62), 249 (0.54), 270 (31), 483 (66), 556 (59), 627 (0.023), 929 (43), 979 (2.0), 1019 (30), 1449 (0.14), 1819 (65), 2034 (120), 3121 (6.9), 3193 (1.9)	[38.557]
	Al^+	57 (1.7), 62 (2.9), 208 (2.1), 213 (1.8), 242 (194), 440 (0.030), 468 (0.23), 800 (89), 872 (15), 894 (167), 1290 (12), 1732 (218), 2170 (641), 2979 (260), 3066 (72)	[36.173]
HCCCN	Na^+	68 (30)*, 219 (49), 254 (0.81)*, 571 (29)*, 806 (36)*, 859 (1.2), 2129 (24), 2357 (435), 3247 (72)	[28.454]
	Mg^+[d]	75 (7.3)*, 264 (0.63)*, 302 (123), 603 (13)*, 751 (32)*, 965 (26), 2188 (5.2), 2387 (749), 3448 (105)	[28.881]
	Al^+	61 (5.3)*, 224 (222), 232 (0.32)*, 526 (3.8)*, 634 (45)*, 893 (43), 1959 (0.032), 2146 (610), 3269 (124)	[26.611]

[a] Calculated vibrational frequencies in cm^{-1}. The values shown were obtained at the MP2(full)/6-31G* level of theory and have been adjusted by a scale factor of 0.9427. [b] IR intensity of the indicated transition, in km mol^{-1}. An asterisk after the value indicates a pair of degenerate vibrational modes. [c] Zero-point vibrational energy, in mHartrees (1 mHartree = 2.6255 kJ mol^{-1}), adjusted by a factor of 0.9661. [d] For H_2CCCC and HCCCN with Mg^+, frequencies, intensities, and ZPE are calculated at B3LYP/6-31G* (uncorrected) instead of MP2(full)/6-31G*.

The present low-temperature RA rate constants are much lower than those estimated in ref 1. Their estimates were extrapolated from high-pressure, high-temperature measured values. The problem does not lie with the comparison of the high-pressure, high-temperature values; for instance, the three-body rate constant for collisional association of Na^+/H_2 in high-pressure He (1 Torr) at 80 K was calculated in the present work to be 3×10^{-31} cm^6 $molec^{-2}$ s^{-1}, compared with the observed value of 1.2×10^{-30} cm^6 $molec^{-2}$ s^{-1} obtained by Smith et al. in the selected ion flow tube (SIFT).[1] The agreement is not perfect, but seems acceptable given the uncertainties of both their experiments and our modeling. This rough agreement at high temperature and pressure encourages confidence in our theoretical framework, and gives at least indirect support to our much smaller estimate of the low-temperature RA rate constant compared with ref 1. The problem arises from the extrapolation they made to low-temperature, zero-pressure conditions. In particular, the lower values assigned here reflect the much lower rate of photon emission calculated for the complex (0.3 s^{-1}), compared with that assumed in ref 1 (100 s^{-1}).

Similar considerations apply to the comparison between our calculated values and the estimates of ref 1 for the low-temperature RA kinetics of Na^+ with CO and N_2, which are not in agreement because of the use of very different photon emission rates. On the other hand, for Na^+ with H_2O agreement is acceptable with their (rather uncertain) value of $(1.6-6.1) \times 10^{-16}$ cm^3 $molec^{-1}$ s^{-1}, reflecting the fact that our calculated photon emission rate of 152 s^{-1} is similar to the assumption of 100 s^{-1} in ref 1. Moreover, for the Na^+/H_2O case, we calculate a rate constant of 1.4×10^{-29} cm^6 $molec^{-2}$ s^{-1} for collisional association in He at 300 K, which is in good agreement with the experimental value of $(7 \pm 3) \times 10^{-30}$ reported in ref 1.

TABLE 5: Some Recent Reported Values of Binding Energies (Bold-Face/Italicized Values Are Experimental, Plain-Face Values Are Computed)

	M = Na		M=Mg		M=Al	
X	MCA(X)[a]	Lit	MCA(X)[a]	Lit	MCA(X)[a]	Lit
H_2	9.4	10.0[b] 10.0[c]	5.8	6.3[d]	3.6	***5.9***[e] 4.4[e]
CO	43.1	***32***[f] ***51***[g]		***42***[y] 42[y]		
N_2	34.2	30.3[h]				
H_2O	95.9	**95**[f] **84**[i] **97**[j] **98**[k] 85−95[f] 89[l]	126.4	***119***[m,y] ***105***[n] 127[o] 119[y]	109.1	***104***[m] 113[p] 121[q]
NH_3	109.5	***102***[f] ***118***[r] ***115***[i] ***103***[l] 97−109[f] 104[l]	154.4	***123***[y] 167[s] 149[y]		
HCN					121.8	***117***[t]
C_2H_2	56.8	50[l]			56.1	***59***[e] 55[u]
C_2H_4	57.6	***43***[f] 46−57[f] 52[l]	73.6	***68***[v] 84[v] ∼75[w]	56.6	**63**[e] **36**[x] 53[x] 60[u]

[a] Calculated metal cation affinity, in kJ mol^{-1}, of the ligand X (present work) (Zero−Kelvin dissociation energies). [b] Ref 67, D_e corrected to D_o using frequencies from the present work. [c] Ref 68, D_e corrected to D_o using frequencies from the present work. [d] Ref 69. [e] Ref 70, experimental values by equilibrium, along with quantum chemical results. [f] Ref 55, experimental values by threshold collisional dissociation; theoretical values using a variety of ab initio and density functional methods. G2 values are in good agreement with the present calculations. [g] Ref 71, experimental values by equilibrium. [h] Ref 72, coupled cluster (CCSD(T)) ab initio calculation, corrected for ZPE effects. [i] Ref 73, experimental values by threshold collisional dissociation. [j] Ref 74, experimental values by equilibrium. [k] Ref 75, experimental values. [l] Ref 56 corrected to 0 K. Experimental values by high pressure mass spectrometry (HPMS) equilibrium; theoretical values by MP2 ab initio. [m] Ref 57, experimental values by threshold collisional dissociation. [n] Ref 76, experimental values by photodissociation. [o] Ref 77, ab initio calculations. [p] Ref 78, ab initio calculations. [q] Ref 79, ab initio calculations. [r] Ref 80, experimental values by equilibrium. [s] Ref 81, density functional calculations. [t] Ref 53, experimental values from equilibrium; ab initio calculations. [u] Ref 82, ab initio calculations. [v] Ref 59, experimental value by photofragmentation spectroscopy; ab initio CISD value. [w] Ref 83, ab initio calculations. [x] Ref 60, this experimental value by photofragmentation spectroscopy, although low, is in agreement with the present assignment within the combined uncertainties of the respective methods; ab initio QCISD(T) value. [y] Ref 58, experimental values by threshold CID. MP2 ab initio calculations.

A further point of contact between the present calculations and high-pressure association experiments is provided by the recent SIFT measurements of Milburn et al.[61] Their value of 4.1 × 10^{-12} cm^3 molec^{-1} s^{-1} for Mg^+ associating with NH_3 at 0.35 Torr of He is in order-of-magnitude agreement with the prediction of 1.3 × 10^{-12} using the present theoretical approach. They observed no association of Mg^+ with H_2, N_2, CO, or H_2O under these conditions. Of these latter molecules only H_2O is predicted to be anywhere close to their detection limits. (For CO, we predict a rate constant of 2.5 × 10^{-15} cm^3 molec^{-1} s^{-1}, which would be unobservable, and H_2 and N_2 are much lower). However, for H_2O, we predict a rate constant of 3.4 × 10^{-13} cm^3 molec^{-1} s^{-1}, which is substantially faster than their indicated detection limit of 10^{-14}. It is thus surprising that they did not observe this reaction. It would be necessary to reduce the Mg^+/H_2O binding energy by almost half to drop our predicted rate below their reported detection limit. In earlier work on this reaction under similar high-pressure conditions, Linder et al.[62] also reported it to be unobservably slow, but Harms et al.[63] reported observing this process. Neither of these latter studies gave quantitative rate information. Although this reaction is certainly not fast, the failure of the most recent experimental studies to observe it is at odds with the theoretical prediction, and remains puzzling.

Implications for Interstellar Cloud Chemistry

In Table 7, we compare calculated reaction rates for the reactions of various interstellar cloud constituents with the metal ions Na^+, Mg^+, and Al^+. These reaction rates are computed using our RA rate coefficients and reactant neutral abundances obtained either from observational studies of TMC-1 or, for species not yet detected within interstellar clouds, from the New Standard Model,[64] in which we have used the abundances at 3 × 10^5 years.

Fast RA combination of metal ions with H_2 would have important consequences for interstellar chemistry modeling, because H_2 is by far the most abundant molecule present, and is relatively difficult to convert to higher molecularity species. Smith et al.[1] estimated a Na^+/H_2 RA rate constant of 4.4 × 10^{-19} at 20 K, and argued that this was on the borderline of possible chemical importance. However, as noted above, their RA rate estimates were made using photon emission rates considerably higher than those calculated here. Accordingly, the rate constants derived here are considerably lower, and the H_2 reactions in Table 6 are all very slow. It seems unlikely that the H_2 RA pathway for any of these metal ions has interstellar chemical importance.

Conventional modeling gives a time scale on the order of 10^6 years for the evolution of the chemical composition of typical dense interstellar clouds such as TMC-1 from initial conditions to steady-state conditions.[64] Moreover, the depletion of atomic metal ions by recombination with free electrons has a similar time scale. Thus 10^6 years is a yardstick for assessing the possibility that the RA of these metal ions with neutral constituents of the clouds plays a major role in the evolution of the chemistry involving these metal ions. It is apparent from Table 7 that radiative recombination is slow on this time scale for H_2 and for most of the other molecules considered here. Only a few RA reactions, involving the largest and most strongly bound complexes in this set, have time constants within 2 orders of magnitude of 10^6 years.

In general, the RA rate constants rise with increasing size of the neutral partner, while at the same time the interstellar abundance falls. As suggested by Table 7, the rise in rate constants tends to outweigh the fall in abundance, so that the larger neutrals give the shortest time scales for depletion of M^+ by RA. This generalization applies up to the point (approached for the largest species in Table 6) at which the RA is so fast that it occurs on virtually every collision (i.e., k_{ra} of about 10^{-9}). This process is thus likely to have the greatest importance for molecules somewhat, but not greatly, larger than those considered in the present work. Molecules likely to be important in

TABLE 6: Radiative Association Rate Constants for Metal Ions Associating with Various Neutrals, along with Estimates of the Dependence on Temperature and on Binding Energy of the Complex and Estimates of the IR Photon Emission Rates from the Metastable Complexes

		M = Na			M = Mg			M=Al		
X		k_{ra} (T)	slope[a]	k_{emit}[b]	k_{ra} (T)	slope[a]	k_{emit}[b]	k_{ra} (T)	slope[a]	k_{emit}[b]
H_2	(10 K)	1.4 (−22)	8	0.3	1.3 (−22)	27	0.07	1.3 (−23)	75	0.03
	(30 K)	8.7 (−23)			8.2 (−23)			8.6 (−24)		
	(100 K)	6.0 (−23)			4.8 (−23)			4.5 (−24)		
CO		1.0 (−19)	2.9	1.1	1.7 (−19)	2.4	2.4	6.7 (−20)	3.2	1.2
		2.0 (−20)			3.5 (−20)			1.3 (−21)		
		3.5 (−21)			6.1 (−21)			2.2 (−21)		
N_2		5.9 (−20)	4.6	1.0	1.5 (−19)	2.2	1.6	2.0 (−20)	5.6	0.6
		1.2 (−20)			3.0 (−20)			4.1 (−21)		
		2.0 (−21)			5.1 (−21)			6.9 (−22)		
H_2O		2.3 (−15)	2.0	152	1.0 (−14)	1.6	254	4.4 (−15)	1.8	229
		2.5 (−16)			1.2 (−15)			5.2 (−16)		
		2.4 (−17)			1.1 (−16)			5.4 (−17)		
NH_3		4.3 (−15)	1.8	97	3.2 (−14)	1.7	160	1.9 (−14)	1.8	163
		4.8 (−16)			3.8 (−15)			2.2 (−15)		
		4.4 (−17)			3.5 (−16)			2.0 (−16)		
HCN		3.8 (−16)	1.8	43	3.1 (−15)	1.8	165	1.9 (−15)	1.8	85
		7.4 (−17)			6.1 (−16)			3.7 (−16)		
		1.2 (−17)			1.0 (−16)			6.2 (−17)		
HNC		1.8 (−15)	1.8	114	5.7 (−15)	1.7	200	6.7 (−15)	2.1	233
		3.6 (−16)			1.1 (−15)			1.3 (−15)		
		5.7 (−17)			1.9 (−16)			2.3 (−16)		
C_2H_2		3.2 (−16)	3.7	22	1.4 (−15)	2.9	27	6.1 (−16)	3.7	24
		6.3 (−17)			2.7 (−16)			1.2 (−16)		
		1.1 (−17)			4.8 (−17)			2.2 (−17)		
C_2H_4		4.3 (−16)	4.0	8	1.6 (−15)	3.0	18	1.5 (−15)	3.7	14
		5.0 (−17)			1.9 (−16)			1.9 (−16)		
		4.9 (−18)			1.8 (−17)			1.9 (−17)		
c−C_3H_2		3.2 (−13)	1.8	26	4.0 (−12)	1.7	50	2.7 (−12)	1.7	54
		3.5 (−14)			5.2 (−13)			3.1 (−13)		
		3.3 (−15)			4.1 (−14)			2.8 (−14)		
H_2CCC		1.7 (−12)	2.0	56	2.8 (−10)	1.6	165	4.0 (−11)	1.8	98
		2.0 (−13)			3.4 (−11)			4.6 (−12)		
		1.8 (−14)			3.0 (−12)			4.2 (−13)		
H_2CCCC		1.1 (−10)	2.4	119	1.5 (−11)	2.2	43	5.0 (−9)	1.8	213
		1.3 (−11)			1.8 (−12)			6.3 (−10)		
		1.2 (−12)			1.6 (−13)			6.0 (−11)		
HCCCN		4.3 (−13)	2.4	50	3.5 (−12)	2.2	114	7.1 (−12)	2.2	91
		6.3 (−14)			7.2 (−13)			1.4 (−12)		
		1.4 (−14)			1.2 (−13)			2.4 (−14)		

[a] Factor by which the rate constant increases if the binding energy is raised by 10 kJ mol^{-1}. [b] IR photon emission rate for the metastable ion−neutral complex with no excess internal energy beyond the energy of binding.

TABLE 7: Estimated Lifetimes of Metal Ions against RA with Various Partners

		M$^+$ lifetime (years)		
	abundance (cm^{-3})	M = Na	M = Mg	M = Al
H_2	1.0 (4)	2 (10)	2 (10)	2 (11)
CO	4 (−1)[a]	8 (11)	5 (11)	1 (12)
N_2	1.2 (−2)[b]	4 (13)	1 (13)	1 (14)
H_2O	5.7 (−3)[b]	3 (9)	5 (8)	1 (9)
NH_3	1 (−4)[a]	8 (10	1 (10)	2 (10)
HCN	1 (−4)[a]	4 (11)	1 (11)	2 (11)
HNC	1 (−4)[a]	1 (11)	6 (10)	6 (10)
C_2H_2	4.4 (−4)[b]	5 (11)	5 (10)	1 (11)
C_2H_4	5 (−7)[b]	5 (14)	5 (13)	6 (13)
c-C_3H_2	1.5 (−4)[a]	4 (8)	6 (7)	8 (7)
H_2CCC	5 (−6)[c]	2 (9)	2 (7)	2 (8)
H_2CCCC	5 (−6)[d]	6 (7)	4 (8)	2 (7)
HCCCN	3 (−5)[a]	6 (8)	4 (8)	2 (8)
e^-	5.4 (−4)[b]	5 (6)[f]	2 (6)[f]	2 (6)[e]

[a] Observed abundance in TMC-1. [b] Modeled at early times (3 × 10^5 years). [c] Estimated from data in ref 85 from TMC-1 observations. [d] Observed abundance in TMC-1. [e] Estimated. [f] Rate constants from ref 86.

this regard include cyanopolyynes, polyynes (polyacetylenes), and PAHs. The relevance of M$^+$ + PAH reactions, as potential loss processes for atomic metal ions, has already been noted in other studies,[15,19,65] and some laboratory data on adducts of M$^+$ with PAHs already exist.[12,13,15,65,66] While much less currently is known regarding reactions of M$^+$ with cyanopolyynes or polyynes, a theoretical study of the RA kinetics for such molecules is in progress.

Several of the reactions modeled here have been considered in the context of the chemical evolution of the outflowing material in the circumstellar envelope IRC+10216. In the course of a recent analysis of this chemistry,[10] estimates were made for the RA rate constants of HCN with Na$^+$, Mg$^+$, and Al$^+$, of HNC with Mg$^+$, and of HC_3N with Na$^+$. The present calculations, using a more satisfactory approach, are in excellent agreement with these estimates for all except Na$^+$/HCN, for which the present estimate is a factor of 3 lower. Thus the present work reinforces the conclusions of ref 10 that these reactions are probably not significant in the formation of metal cyanides, but reactions with larger cyanopolyynes may be important. Accurate modeling for the larger cyanopolyynes is in progress, as noted above. On the other hand, the present value is much smaller than an estimate in the same study[10] of the rate of association of NH_3 with Na$^+$ (1 × 10^{-10} cm^3 molec^{-1} s^{-1}), and it now seems unlikely that this reaction could have any chemical importance in this environment. Similarly, the comparatively low association rate coefficients calculated for NH_3 with Mg^+ and with Al^+ appear to rule out the proposed formation by these reactions of $MgNH_2$,[10,61] MgNH,[10] or $AlNH_2$[10] within IRC+10216.

Although the present work (and the discussion above) is concerned solely with reactions of M^+ with closed-shell molecules, several abundant interstellar radicals, such as O_2, CN, C_2H, and C_4H, may also play a part here. Chemical intuition suggests that the binding energies of radical M^+ ions, such as Mg^+ and Ca^+, with radical neutrals X to form 'spin-paired' adducts, such as singlet $MgCCCCH^+$, should be quite large, whereas binding energies of singlet M^+ − Na^+, Al^+, and K^+ − to these neutrals should be markedly lower. Some preliminary calculations (Petrie, unpublished results) support this notion, indicating that the binding energies of singlet adducts of Mg^+ with interstellar radicals are significantly higher than the corresponding values for doublet adducts of Na^+ and Al^+, and for any of the adducts (formed from closed-shell neutrals) surveyed in Table 1. It may well be that reactions of M^+ with interstellar radicals (which are often present in abundances comparable with their closed-shell analogues) provide an important additional pathway to depletion of Mg^+ and similar ions, but not of singlet ions such as Na^+ and Al^+.

Conclusions

The RA reactions studied here are mostly predicted to be too slow to have significance in the chemical evolution of the metal components of typical interstellar clouds as they are currently modeled. However, some of the largest and most strongly bound complexes are formed with time constants shorter than the cloud lifetime (10^8 years), and could provide routes to the synthesis of complex metal-containing molecules in the later life of the clouds. Neutral partners larger than those considered here are expected to have shorter time scales for radiative association at typical cloud abundances, and this process may be important for them on the time scale of chemical evolution of the clouds (10^6 years).

For circumstellar envelopes typified by the object IRC+10216, the rate of chemical evolution and the molecular densities are both higher than in clouds such as TMC-1, but the conclusion is similar, namely that the reactions considered in the present work are too slow to have importance in the chemical evolution of the metals, but that radiative association with somewhat larger neutrals is likely to be fast enough to be significant.

This study has found that some RA reactions, which have previously been suggested to be fast enough to be important in cloud evolution, notably the Na^+/H_2 association, are slower than previously suggested.

The set of computed binding energies reported here agrees acceptably well with the bulk of prior calculations for various previously reported complexes. Recent experimental results have also tended to converge toward the quantum chemical values; and it appears that, for these small nontransition metal cations binding to small neutral partners, binding energies can be confidently estimated within perhaps 10 kJ mol^{-1} at the theoretical level of G2 theory or density functional theory with an adequate basis.

Although it was not the focus of the present study, the computational approach also gives predictions of three-body reaction kinetics at the high pressures of flowing afterglow, SIFT, or drift tube instruments. Several comparisons of reported values with the present set of reactions showed order-of-magnitude agreement. The outstanding exception is the Mg^+/H_2O association, which is predicted to be more than an order of magnitude faster than a recent experimental observation.

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