

## MOLECULAR CLUSTERS IN INTERSTELLAR CLOUDS

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### ABSTRACT

Cluster ions of the type  $\text{H}_3^+ \cdot (\text{H}_2)_p$ ,  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q$ , and mixed clusters of the type  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q (\text{H}_2)_p$  may be formed by gas-phase chemistry or by cosmic-ray-induced desorption from dust grains in dense interstellar clouds. An analysis of formation mechanisms leads to the prediction of an equilibrium abundance of  $\text{H}_3^+ \cdot (\text{H}_2)_p$  clusters, where  $p = 3-4$ , of  $\sim 10^{-10} n$ . The initial stage in the gas-phase formation of these cluster ions would be via radiative association of  $\text{H}_3^+$  and  $\text{H}_2$  at a rate  $\sim 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ . Desorption from  $\text{H}_2$  monolayers by  $\text{H}_3^+$  or  $\text{He}^+$  collisions with grains leads to a similar production rate for  $\text{H}_3^+ \cdot (\text{H}_2)_p$  clusters. Such cluster ions have been observed in laboratory experiments on charged particle impact with solid  $\text{H}_2$  layers. Cosmic-ray sputtering of adsorbed layers on dust can form cluster ions via the creation of energetic ions such  $\text{H}_3^+$  and  $\text{H}_3\text{O}^+$ . An equilibrium abundance of  $\text{H}_3^+ \cdot (\text{H}_2)_p$  clusters, independent of cloud density, of  $\sim 10^{-8} \text{ cm}^{-3}$  is predicted due to cosmic-ray sputtering of adsorbed  $\text{H}_2$  molecules. Sputtering of ice layers by cosmic rays should produce a range of large cluster ions  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q$  in interstellar clouds. Laboratory data on sputtering of  $\text{H}_2\text{O}$  with keV  $\text{He}^+$  ions shows that clusters with  $q \lesssim 50$  are possible. The fragmentation of such clusters on electron-ion recombination is likely to lead to a range of neutral clusters. The abundance of such clusters, which may be considered to be a population of very small grains, is predicted to be comparable to that of dust grains. These clusters can accrete other atomic and molecular species and may constitute a gas-phase route toward grain formation in dense interstellar clouds.

*Subject headings:* ISM: abundances — ISM: molecules — molecular processes

### 1. INTRODUCTION

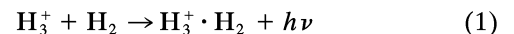
The freeze-out, reaction, and desorption of atoms and molecules on dust grains in interstellar clouds under a variety of conditions has important consequences in interstellar chemistry (Williams 1993; Charnley, Tielens, & Millar 1992) and yet is poorly understood. Desorption processes, such as grain-grain collisions in shocks (Jones et al. 1994), or cosmic-ray heating (Léger, Jura, & Omont 1985), are assumed to lead to the liberation of *individual* atoms and molecules even under conditions where the energetics of such processes permit several molecules to be desorbed. The rapid ejection of molecules from a solid surface in an energetic event is well known to result in cluster formation rather than the liberation of individual molecules (Sugano 1991). Such clusters have been observed to be emitted from solid  $\text{H}_2$  (Clampitt & Gowland 1969) and  $\text{H}_2\text{O}$  ice (Floyd & Prince 1972) under low-energy electron impact and from a variety of other materials under ion impact (Lancaster et al. 1979). An extensive literature exists on the physical properties and formation of neutral molecular clusters and cluster ions (Sugano 1991; Haberland 1994).

The surface of dust grains in dense interstellar clouds is known to accrete a variety of ices, including  $\text{H}_2\text{O}$  and CO (Whittet 1992). These ices will contain an appreciable quantity of dissolved  $\text{H}_2$  (Sandford & Allamandola 1993) and are likely also covered with a monolayer of adsorbed  $\text{H}_2$ . Desorption from this surface layer is potentially a source of  $\text{H}_2$  clusters, while the disruption of  $\text{H}_2\text{O}$  and CO coatings on dust will also lead to cluster formation. In this paper, I examine the role that chemical reactions, cosmic-ray heating, and shocks play in the formation of molecular clusters in interstellar clouds and show

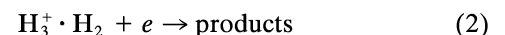
that such clusters can exist at a significant concentration in the gas phase in dense clouds.

### 2. FORMATION AND GROWTH OF $\text{H}_2$ CLUSTERS

Clustering of  $\text{H}_2$  molecules on  $\text{H}_3^+$  ions is observed under conditions where  $\text{H}^+$  ions are formed in a high-pressure ambient of  $\text{H}_2$  (Clampitt & Gowland 1969; Beuhler & Friedman 1982). Under interstellar conditions,  $\text{H}_3^+ (\text{H}_2)_n$  clusters can be created by both gas-phase and grain reactions mediated by cosmic-ray ionization. In the gas phase, the primary reaction

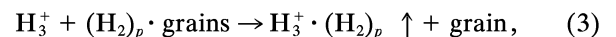


will proceed at the rate of a slow radiative association, i.e.,  $k_1 \sim 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  with the cluster destroyed in the reaction



at a rate  $k_2 \sim 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ . Then, in equilibrium,  $[\text{H}_3^+ \cdot \text{H}_2] / n \sim 10^{-10}$ .

Such clusters could also be formed in collisions of  $\text{H}_3^+$  with cold dust grains in dark clouds. As noted by Sandford & Allamandola (1993), ice-coated grains will be covered with up to a monolayer ( $\sim 1 \times 10^5 \text{ cm}^{-2}$ ) of adsorbed  $\text{H}_2$ . Then



which is exothermic by

$$\Delta H = \Delta H(\text{cluster}) - p\Delta H(\text{H}_{2\text{ads}}), \quad (4)$$

where  $\Delta H(\text{cluster})$  is the heat of formation of the cluster ion (Table 1) and  $\Delta H(\text{H}_{2\text{ads}})$  is the adsorption energy of an  $\text{H}_2$  molecule on the surface of an ice-coated grain. For  $\text{H}_2 \cdot \text{H}_2\text{O}$  this is  $\sim 555 \text{ K}$  (Sandford & Allamandola 1993). A similar value is obtained for  $\text{H}_2 \cdot \text{CO}$ . For simplicity, all values of  $\Delta H$

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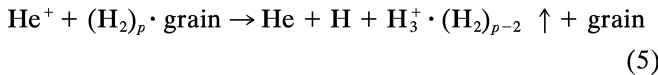
TABLE 1  
 $\Delta H$  FOR ADDITION OF  $H_2$  TO  $H_3^+ \cdot (H_2)_p$   
 CLUSTER IONS

$p$ for Reaction $H_3^+ \cdot (H_2)_p + H_2 \rightarrow H_3^+ \cdot (H)_{p+1}$	$\Delta H$ ( $10^3$ K)
0.....	4.3
1.....	1.8
2.....	1.6
3.....	0.9

NOTE.—Data from Hiraoka & Kebarle 1975 as corrected by Huber 1980.

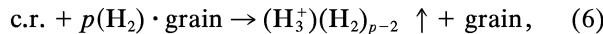
will be expressed in kelvins. The cluster ion formation rate via reaction (3) is  $k_3 = v_{H_3^+}^+ \pi a^2 S_p \text{ cm}^3 \text{ s}^{-1}$ , where  $v_{H_3^+}^+$  is the speed of an  $H_3^+$  ion,  $a$  is the grain radius, and  $S_p$  is the probability factor for a reaction leading to ejection of a cluster containing  $p$   $H_2$  molecules. Steric and bonding considerations would suggest  $p \sim 6$  (Clampitt & Gowland 1969; Hiraoka & Kebarle 1975; Huber 1980). For grains with  $a = 10^{-6}$  to  $10^{-5}$  cm, and a gas kinetic temperature  $T = 30$  K,  $k_3 = 1.4 \times (10^{-7} \text{ to } 10^{-5}) S_p \text{ cm}^3 \text{ s}^{-1}$ , with clusters destroyed by electron-ion recombination (reaction [2]). The equilibrium concentration of cluster ions containing  $p$   $H_2$  molecules is  $[H_3^+ \cdot (H_2)_p]/n \sim 10^{-10} S_p$ , where an integrated grain area  $\pi a^2 n_g = 2.1 \times 10^{-21} n \text{ cm}^2 \text{ cm}^{-3}$  has been used (Duley & Williams 1984) with  $k_2 = 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ . The value of  $S_p$  is uncertain but could be  $\sim 0.3$  as in the grain-catalyzed reaction to form  $H_2$ .

Since  $[He^+] \approx [H_3^+] \approx 10^{-8} n$  in dark clouds,  $He^+$  is also likely to participate in cluster ion formation via the reaction



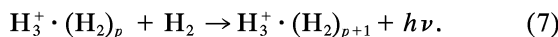
at a rate similar to that of reaction (3).

An additional reaction channel will arise from direct cosmic-ray ionization of  $H_2$  molecules adsorbed on grains,



which occurs at the canonical cosmic-ray ionization rate  $\sim 10^{-17} \text{ s}^{-1}$  per  $H_2$  molecule (Duley & Williams 1984). With an integrated grain area of  $2.1 \times 10^{-21} n \text{ cm}^2 \text{ cm}^{-3}$  and a surface coverage  $x \times 10^{15} \text{ cm}^{-2}$ , where  $0 \leq x \leq 1$ , the formation rate of the gas-phase cluster is  $\approx 2 \times 10^{-23} x n \text{ cm}^{-3} \text{ s}^{-1}$ . With  $[e] = 10^{-8} n$  and  $k_2 = 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ ,  $[H_3^+ \cdot (H_2)_{p-2}] \sim 2 \times 10^{-9} x \text{ cm}^{-3}$ .

Gas-phase  $H_3^+ \cdot (H_2)_p$  clusters will combine with  $H_2$  to form larger clusters in the exothermic reaction



The rate constant for radiative association is again uncertain but could approach that for large polyatomic molecules ( $k_7 = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) if  $p \gg 1$ . I will assume a rate  $k_7 \sim 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  intermediate between this value and that assumed for reaction (1). As  $k_7[H_2] \gg k_6[e]$  in dense clouds, the equilibrium in reaction (7) shifts rapidly ( $\sim 10^8$  s) to larger clusters. Since  $\Delta H$  for reaction (7) decreases with  $p$  (Table 1), an equilibrium cluster size will be reached when

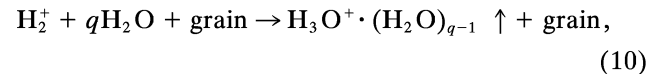
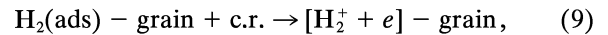
$$A \exp[-\Delta H/kT] = k_7 n/2, \quad (8)$$

which expresses an equality between dissociation of the cluster at the gas kinetic temperature,  $T$ , and the growth rate by addition of  $H_2$ . With  $A \sim 7.5 \times 10^{12} \text{ s}^{-1}$  (Sandford & Alla-

mandola 1993),  $T = 30$  K,  $k_7 = 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , and  $n = 3 \times 10^4 \text{ cm}^{-3}$ , this equality is reached when  $\Delta H = 1430$  K and is half this value at  $T = 15$  K. This suggests that the equilibrium size for  $H_3^+ \cdot (H_2)_p$  clusters in dense clouds has  $p = 3-4$  (Table 1).

### 3. FORMATION AND GROWTH OF $H_2O$ AND $CO$ CLUSTERS

Sputtering of  $CO$  and  $H_2O$  solids by cosmic-ray impact, which has been proposed as a desorption mechanism for molecules on dust grains (Léger et al. 1985), provides a mechanism for the creation of cluster ions such as  $H_3O^+ \cdot (H_2O)_n$  and  $H_3O^+ \cdot (CO)_n$ . Ejection of water cluster ions from ice under particle impact is well documented (Floyd & Prince 1972; Tantsynev & Nikolaev 1972). In interstellar clouds, ions such as  $H^+$ ,  $H_3^+$ , and  $H_3O^+$  will be created in ices by cosmic-ray ionization of adsorbed  $H_2$  or by dissociative ionization of  $H_2O$ . The rate for formation of such ions will be  $\sim 10^{-17} \text{ s}^{-1}$  (H nucleus) $^{-1}$ . Then



where the size of the cluster ion ejected will depend on the kinetic energy of the  $H_2^+$  produced in the primary interaction and the stability of the resulting cluster. Lancaster et al. (1979) have observed clusters with  $\leq 50$   $H_2O$  molecules on irradiation of ice with 3 keV  $He^+$  ions, while Floyd & Prince (1972) report the ejection of clusters containing up to 8  $H_2O$  molecules from ice bombarded with 80 eV electrons.  $H^+ \cdot (H_2O)_q$  clusters with  $q = 21$  and 28 are found to be particularly stable (Nagashima et al. 1986). The formation rate of  $H_3O^+ \cdot (H_2O)_{q-1}$  clusters is then  $1.7 \times 10^{-22} n l f_q \text{ cm}^{-3} \text{ s}^{-1}$ , where  $l$  is the number of monolayers of ice on dust and  $f_q$  is the probability per cosmic-ray ionization that a cluster with  $q$   $H_2O$  molecules is ejected. With destruction of clusters by electron-ion recombination, the equilibrium abundance of water cluster ions is  $1.7 \times 10^{-8} l f_q \text{ cm}^{-3}$ , independent of density.

Ionized  $H_2O$  clusters will grow by addition of  $H_2$ ,  $CO$ , and other molecules in interstellar clouds. Hybrid cluster ions such as  $H_3O^+ \cdot (H_2O)_q \cdot H_2$  have been observed in laboratory experiments (Okumura et al. 1986). Assuming accretion by radiative association at a rate  $10^{-12} n(H_2) \text{ s}^{-1}$ , ionized  $H_2O$  clusters will rapidly attach a layer of  $H_2$  molecules.  $CO$  will also be accreted by these ions to form hybrid  $H_3O^+ \cdot (H_2O)_q \cdot H_2 \cdot CO$  clusters.

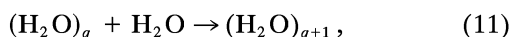
### 4. NEUTRAL CLUSTERS

Electron-ion recombination involving cluster ions is unlikely to result in total fragmentation, with the result that destruction of ionized clusters may reasonably be expected to lead to a size distribution of smaller neutral clusters. In the case of  $(H_2)_p$  clusters, the small binding energy of  $H_2$  ( $\Delta H \sim 100$  K; Sandford & Allamandola 1993) and the large zero-point energy for such light molecules will result in rapid thermal dissociation, even at gas kinetic temperatures as low as 10 K (eq. [8]). This situation will be quite different, however, for  $(H_2O)_q$  clusters where binding energies are typically  $\sim 2300$  K per  $H_2O$  molecule (Floyd & Prince 1972). Such clusters will be stable against vaporization in dense clouds and may grow by accretion of other gaseous components including  $H_2O$ ,  $CO$ ,

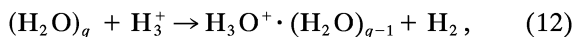
TABLE 2  
SUMMARY OF FORMATION RATES AND EQUILIBRIUM ABUNDANCES FOR SIMPLE CLUSTER IONS IN DENSE  
( $n \geq 10^4 \text{ cm}^{-3}$ ) INTERSTELLAR CLOUDS

Cluster Ion	Formation Rate ( $\text{cm}^{-3} \text{ s}^{-1}$ )	Rate/Parent Ion ( $\text{s}^{-1}$ )	Equilibrium Abundance ( $\text{cm}^{-3}$ )	Reaction
$\text{H}_3^+ \cdot \text{H}_2$ .....	$10^{-24} nn(\text{H}_2)$	$10^{-16} n(\text{H}_2)$	$10^{-10} n$	(1)
$\text{H}_3^+ \cdot (\text{H}_2)_p$ .....	...	$10^{-12} n(\text{H}_2)$	...	(1), (7)
$\text{H}_3^+ (\text{H}_2)_p$ .....	$10^{-16} nn(\text{H}_3^+)S_p$	...	$10^{-10} S_p$	(3)
	$10^{-16} nn(\text{He}^+)S_p^1$	...	$10^{-10} S_p^1$	(5)
$\text{H}_3^+ (\text{H}_2)_{p-2}$ .....	$1.7 \times 10^{-23} xn$	...	$1.7 \times 10^{-8} x$	(6)
$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_{q-1}$ .....	$1.7 \times 10^{-22} nlf_q$	...	$1.7 \times 10^{-8} lf_q$	(9), (10)
$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_{q-1} \cdot \text{H}_2$ .....	...	$10^{-12} n(\text{H}_2)$	...	...

$\text{H}_2\text{CO}$ , etc. For example, when  $q \gg 1$ , the accretion of additional  $\text{H}_2\text{O}$ ,



should proceed at or near the kinetic rate ( $k_{11} \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ). With  $[\text{H}_2\text{O}]/n \sim 10^{-6}$  as indicated from models of dense cloud chemistry (Willacy & Williams 1993), large  $\text{H}_2\text{O}$  clusters will experience rapid growth. Destruction will be by reaction with ions such as  $\text{H}_3^+$ ,



followed by fragmentation on electron-ion recombination. The overall effect of these two processes, if it is assumed that fragmentation leads to the creation of several smaller clusters, is to increase the concentration of clusters in the gas in dense clouds. The relative rate of reactions (11) and (12) is  $k_{11}[\text{H}_2\text{O}]/k_{12}[\text{H}_3^+]$  with fragmentation occurring over a timescale  $t_f = 10^6/[e] \sim 10^{14}/n \text{ s}$ . At typical dense cloud densities ( $n = 3 \times 10^4 \text{ cm}^{-3}$ ),  $t_f = 3 \times 10^9 \text{ s}$ . Then the doubling time for cluster concentration will be  $t_d = (k_{12}[\text{H}_3^+])^{-1} \sim 10^{17}/n = 3 \times 10^{12} \text{ s} \sim 0.1 \text{ Myr}$ . Given this short doubling time, it is apparent that a significant concentration of  $(\text{H}_2\text{O})_q$  clusters is expected in dense clouds. As an example, with initial cluster formation via reactions (9) and (10) and assuming  $lf_q \sim 1$ , cluster ions are formed at the rate  $10^{-22} n \text{ cm}^{-3} \text{ s}^{-1}$  with an equilibrium abundance  $\sim 10^{-8} \text{ cm}^{-3}$ . At a doubling time of 0.1 Myr as above, the abundance of neutral  $\text{H}_2\text{O}$  clusters will increase to  $(10^{-5} \text{ to } 10^{-2}) \text{ cm}^{-3}$ , over a 1–2 Myr timescale, respectively. With  $n = 3 \times 10^4 \text{ cm}^{-3}$ , abundances relative to hydrogen would then be  $3 \times 10^{-10}$  to  $3 \times 10^{-7}$ , comparable to those of dust grains. At a growth rate of  $\sim 3 \times 10^{-11} \text{ s}^{-1}$ , such clusters will contain  $\sim 100$   $\text{H}_2\text{O}$  molecules after 1 Myr, in addition to other accreted molecules such as CO.

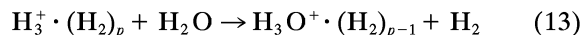
## 5. CARBON CLUSTERS

Cosmic-ray sputtering of carbonaceous coatings on silicate dust will result in the ejection of hydrocarbon components directly into the gas phase in interstellar clouds. A study of cluster formation arising from the impact of  $\text{He}^+$  ions on condensed benzene,  $\text{C}_6\text{H}_6$ , and cyclohexane,  $\text{C}_6\text{H}_{12}$ , solids at 77 K shows a range of ion products extending from  $\text{CH}^+$  to  $\text{C}_n\text{H}_m^+$  containing in excess of 25 carbon atoms (Lancaster et al. 1979). Multiatom hydrocarbon clusters are then expected from cosmic-ray sputtering of carbonaceous grains in interstellar clouds with the generation rate of these clusters similar to that for  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q$  cluster ions. These clusters will frag-

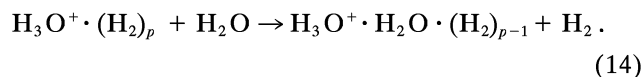
ment due to electron-ion recombination, yielding a range of smaller clusters which can continue to grow by reaction with gas-phase molecules. Large clusters will be resistant to destruction, as they will have many internal vibrational modes that can distribute and delocalize excess energy. Such clusters would have similar properties to small grains.

## 6. DISCUSSION

A summary of projected cluster-ion formation rates in dense clouds is given in Table 2 and shows that a variety of such molecules should be present at low relative abundance in dense interstellar clouds. Formation rates and derived equilibrium abundances are, however, uncertain in the absence of accurate rate constants for the reactions involved. The most abundant cluster ions are predicted to be of the type  $\text{H}_3^+ \cdot (\text{H}_2)_p$  with  $p = 3-4$ . These will be present at a fractional abundance of  $\sim 10^{-10} n$  even if  $k_1$  is as small as  $10^{-16} \text{ cm}^3 \text{ s}^{-1}$ . A background abundance amounting to  $10^{-10}$  to  $10^{-11} \text{ cm}^{-3}$  can also be produced by grain processes, including cosmic-ray sputtering of adsorbed  $\text{H}_2$ . If the reaction



occurs at a rate exceeding  $\sim 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , then this channel would efficiently convert hydrogen-based clusters to  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q \cdot \text{H}_2$  through



This reaction should proceed at the kinetic rate,  $k_{14} \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The equilibrium abundance of  $\text{H}_3\text{O}^+ \cdot (\text{H}_2)_{p-1}$  clusters is approximately  $k_{13}[\text{H}_2\text{O}][\text{H}_3^+ \cdot (\text{H}_2)_p]/k_2[e] \sim 10^{-11} n$ , while that of the  $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} \cdot (\text{H}_2)_p$  adduct is  $\sim 10^{-12} n$ , assuming  $[\text{H}_2\text{O}] = 10^{-6} n$ . The relative abundance of larger  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q \cdot \text{H}_2$  clusters decreases by a factor of 10 for each additional  $\text{H}_2\text{O}$  molecule. IR spectra of these simple cluster ions have been well characterized (Table 3).

The route to larger  $\text{H}_2\text{O}$ -based clusters would appear to be via cosmic-ray sputtering of ice coatings on grains. Substantial accretion of  $\text{H}_2\text{O}$  ice on dust is indicated from the observation of a  $3.07 \mu\text{m}$  absorption band in dense clouds (Whittet 1992), but it is also clear that some process must limit the growth of ice layers in dense clouds (Williams 1993). Thermal desorption by cosmic-ray heating together with initiation of an exothermic chemical reaction in grain mantles has been suggested (Léger et al. 1985), but the effectiveness of this thermal process may be limited (Willacy & Williams 1993). Cosmic-ray ionization

TABLE 3  
INFRARED ABSORPTION FREQUENCIES FOR SOME MOLECULAR CLUSTER IONS

Ion	Frequency ( $\text{cm}^{-1}$ )	Reference
$\text{H}_5^+$ .....	3522, 3910	Okumura, Yeh & Lee 1985
$\text{H}_7^+$ .....	3980	
$\text{H}_9^+$ .....	4020	
$\text{H}_5\text{O}_2^+$ .....	3528, 3617, 3662, 3693	Yeh et al. 1989
$\text{H}_7\text{O}_3^+$ .....	3642, 3587, 3726	
$\text{H}_9\text{O}_4^+$ .....	3636, 3648, 3723, 3733	

within dense clouds is nevertheless well established, at least as a driving force for ion-molecule chemistry. Ion formation must also occur in ice coatings on dust where the high-density environment ( $3.3 \times 10^{22}$   $\text{H}_2\text{O}$  molecules  $\text{cm}^{-3}$ ) will favor cluster formation. The small thickness of ice layers on dust will also facilitate the ejection of clusters in an analogous way to that observed on keV  $\text{He}^+$  ion impact (Lancaster et al. 1979).

There would therefore appear to be a chemical route to the formation of multimolecule clusters inside dense interstellar clouds which could lead with fractionation to a density of  $10^{-7}$  to  $10^{-10}$  clusters  $\text{cm}^{-3}$  over timescales of  $\sim 1$  Myr. These

clusters are essentially a separate population of very small grains (VSGs), analogous to the carbonaceous VSGs thought to be responsible for the IR cirrus emission. It is unlikely that such cluster ions will be found in appreciable quantities in diffuse clouds, however, as they will be rapidly photodissociated in the ambient UV radiation field (Sugano 1991). IR emission at the frequencies listed in Table 3 may be expected from such regions.

Accretion of other atomic and molecular components by  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_q$  clusters is a potential chemical route to the formation of more refractory clusters in dense clouds, and the addition of C, CH, or  $\text{C}_2\text{H}_2$  molecules could promote the establishment of a carbonaceous network based on valence bonding of carbon. The vaporization of  $\text{H}_2\text{O}$  molecules from this network might leave a residual carbonaceous cluster. Carbonaceous clusters formed in this way would be expected to have rather unique chemical and physical properties.

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