Hydrated sulphuric acid in dense molecular clouds

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Hydrated sulphuric acid in dense molecular clouds

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ABSTRACT

We consider sulphur depletion in dense molecular clouds, and suggest hydrated sulphuric acid, \( \text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O} \), as a component of interstellar dust in icy mantles. We discuss the formation of hydrated sulphuric acid in collapsing clouds and its instability in heated regions in terms of the existing hot core models and observations. We also show that some features of the infrared spectrum of hydrated sulphuric acid have correspondence in the observed spectra of young stellar objects.

Key words: ISM: clouds – dust, extinction – ISM: lines and bands – ISM: molecules – infrared: ISM.

1 INTRODUCTION

Observations of sulphur-bearing and other molecular species in dense molecular clouds have established that elemental sulphur is more depleted by two orders of magnitude than are carbon, oxygen and nitrogen (Joseph et al. 1986; Kemper et al. 1999). Current chemical models of translucent clouds imply that sulphur is depleted by factors exceeding 10 with respect to its average abundance in diffuse clouds, where all the elemental sulphur appears to reside essentially in the gas phase (Snow & Witt 1996).

The supposed large depletion of sulphur relative to the other elements may be illusory as a consequence of the existence of an unobservable form of molecular sulphur, \( \text{S}_2 \), which could be the major carrier of the elemental sulphur. \( \text{S}_2 \) has been suggested to be ubiquitous in comets (A’Hearn et al. 2000), where it could be produced in the innermost coma via fast reactions between OCS and atomic sulphur in the metastable \( ^1\text{D} \) state. In interstellar clouds, the sulphur dimer might attain large abundances in hot cores (Charnley 1997), but its concentration is unlikely to be significant in cold regions (Ruffle et al. 1999).

A possible hypothesis is that the missing sulphur is locked up in icy grain mantles. In star-forming regions, only trace amounts of solid-state sulphur are detected (Palumbo, Geballe & Tielens 1997). Gas-phase chemistry of sulphur- and other molecules implies that S, SO and CS are important reservoirs of sulphur in the gas. Oxidation of these species on grain surfaces will lead to SO2 and OCS, which have both been identified in the grain mantles. The subsequent hydrogenation would lead to the formation of \( \text{H}_2\text{S}, \text{H}_2\text{CS} \) and CH3SH (Palumbo et al. 1997). None of these species is present on the icy surfaces of interstellar grains (Gibb et al. 2000). However, the discovery of iron sulphide, \( \text{FeS} \), in two Herbig stars (Keller et al. 2002) points to a chemistry where the bulk of the sulphur depletion is accomplished by incorporation into dust grains.

There is no strong infrared band that can be assigned to sulphur compounds in icy mantles. Hence the solid-state sulphur must in be in a form which has infrared modes that are (presently) inaccessible, or obscured by much broader spectral features. In this paper, we discuss the depletion of sulphur from the gas phase in the formation on grains of a weakly refractory material, the hydrated sulphuric acid \( \text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O} \).

2 THE FORMATION OF SULPHURIC ACID ON GRAINS

Sulphuric acid aerosols are ubiquitous in our atmosphere and they have been observed also in the atmosphere of Venus (Krasnopolsky 1994). The production of \( \text{H}_2\text{SO}_4 \) is widespread in the terrestrial atmosphere, where it takes place naturally as a consequence of volcanic injection of materials, and anthropogenically from combustion of fuels. Oxidized sulphur forms readily in hydrocarbon combustion where sulphur is a minor impurity in the fuel (Brown et al. 1996a,b). The detailed kinetics of atmospheric sulphuric acid aerosols is uncertain. It appears essential that a surface be available and there is some indication that the chemical composition of the refractory cores is consequential (Brown et al. 1996c). There is little evidence for a strong chemical interaction between carbon particles and \( \text{H}_2\text{SO}_4 \), and it is likely that particulates such as \( \text{SiOH}_n, \text{Fe}_2\text{O}_3 \) and \( \text{MgCO}_3 \) provide a condensed phase for reaction. Therefore in an oxidizing environment there appears to be a ubiquitous chemistry through which sulphur is oxidized to sulphuric acid.

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That much of the sulphur is in the form of $S^+$ ions in translucent clumps led Ruffle et al. (1999) to suggest an enhanced deprotonation rate of sulphur during the clump collapse. Ions collide more rapidly with grains and may stick more efficiently to them than do neutral species. Eventually in the collapse, gas-phase sulphur becomes incorporated in neutral species, still allowing for sulphur-bearing species in dense cores to be detectable. The reaction chain to form sulphuric acid on grain surfaces probably begins with the neutralization of $S^+$ ions which thermalize to the grain temperature $T_d$ and are adsorbed on the surface (Shalabiea & Greenberg 1994), followed by reaction with OH to produce SO. Subsequent reactions with OH end with the formation of sulphuric acid:

$$\text{SO} + \text{OH} \rightarrow \text{SO}_2 + \text{H}, \quad (R_1)$$

$$\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3, \quad (R_2)$$

$$\text{HSO}_3 + \text{OH} \rightarrow \text{H}_2\text{SO}_4. \quad (R_3)$$

The production rate of $\text{H}_2\text{SO}_4$ can be estimated as

$$\frac{d n_{\text{H}_2\text{SO}_4}}{dt} = \eta_1 n_2 n_3 k_0 n_{\text{OH}}, \quad (1)$$

where $n_1$, $n_2$ and $n_{\text{OH}}$ are the surface abundances of $\text{H}_2\text{SO}_4$, sulphur and OH, respectively, $k_0$ is the second-order rate coefficient of the triggering reaction between S and OH, and $\eta_1(2,3)$ is the efficiency of reaction $R_{1(2,3)}$ as the exit channel of $\text{SO(}\text{SO}_2, \text{HSO}_3\text{)}$:

$$\eta_1 = \left(1 + \frac{D_j}{k_0 n_{\text{OH}}}\right)^{-1} \quad (j = 1, 2, 3). \quad (2)$$

In equation (2), $D_j$ ($\text{s}^{-1}$) and $k_0$ ($\text{cm}^3 \text{s}^{-1}$) are the total destruction rate of the sulphur-bearing reactant and the rate coefficient of reaction $R_j$, respectively. We describe the rate coefficients of surface reactions as

$$k_j = \kappa \left(\tau_{\text{hop},j}^{-1} + \tau_{\text{hop},2}^{-1}\right) / \mathcal{N}_d \rho_d \quad (3)$$

(Hasegawa, Herbst & Leung 1992; Herbst 1995), where $\kappa$ is an efficiency factor, $\tau_{\text{hop},j}$ ($\text{s}$) is the time-scale of thermal hopping of the $i$th adsorbed species, $\mathcal{N}_d$ is the number of surface sites, and $\rho_d$ is the grain number density. The hopping rate is given approximately by the expression

$$\tau_{\text{hop},j}^{-1} = v_0 \exp(-E_b/T_d) \quad (4)$$

where $v_0$ is the vibrational frequency of the adsorbate and $E_b$ ($\text{K}$) is the potential barrier between two sites of potential minima. Quantum mechanical tunneling rates are negligible for species heavier than H atoms.

With hopping potential barriers of 330 and 378 K for S and OH, respectively (Hasegawa et al., 1992), we get $\tau_{\text{hop},5} = 4.7 \times 10^{-2} \text{ s}^{-1}$ and $\tau_{\text{hop},\text{OH}} = 3.8 \times 10^{-4} \text{ s}^{-1}$. Then the $\text{H}_2\text{SO}_4$ formation rate in equation (1) becomes

$$\frac{d f_{\text{H}_2\text{SO}_4}}{dt} = \mathcal{R} \sim 1.12 \times 10^{18}\eta^3 f_5 f_{\text{OH}} \text{Myr}^{-1}, \quad (5)$$

where $f_5$, $f_5$ and $f_{\text{OH}}$ are the fractional surface abundances of $\text{H}_2\text{SO}_4$, S and OH, respectively. Following Hasegawa et al. (1992), in equation (5) we set $\kappa \sim 1$ for atoms and radicals involved in the reaction. We adopt $n_x = 1.33 \times 10^{-17} n_H$, where $n_H$ is the concentration of H nuclei in all forms, and $N_d = 10^9$. We approximate the product $\eta_1 f_5 f_{\text{OH}}$ by the cube of an average factor $\eta$. Setting $f_5 \sim 1 \times 10^{-5}$, roughly the cosmic abundance of sulphur (Snow & Witt 1996), and $f_{\text{OH}} \sim 5 \times 10^{-5}$ (Hasegawa et al. 1992), we obtain the formation time

$$\tau_1 \sim \mathcal{R}^{-1} = 1.8 \times 10^{-9} \eta^{-3} \text{ Myr}. \quad (6)$$

This time is less than 1 Myr as long as $\eta \gtrsim 0.001$. The derived lower limits on the reaction efficiencies are plausible since there is no evidence of a significant concentration of sulphur-bearing molecules in interstellar ices (Palumbo et al. 1997; Gibb et al. 2000) or in the gas phase in cold dense clouds.

From heat of vaporization and vapour pressure measurements, the vapour pressure of $\text{H}_2\text{SO}_4$ can be estimated. Extrapolation of the equilibrium vapour pressure from higher pressures to $10^{-20}$ atm leads to an equilibrium temperature of 160 K. The vapour pressure of $\text{H}_2\text{SO}_4$ is much lower than that of $\text{H}_2\text{O}$ (Zhang et al. 1993). Thus, clearly not as refractory as standard minerals, sulphuric acid should not be classified as a volatile species.

Once $\text{H}_2\text{SO}_4$ is formed it acts to remove $\text{H}_2\text{O}$ selectively from the vapour phase. There is a considerable body of evidence showing unit accommodation for $\text{H}_2\text{O}$ on $\text{H}_2\text{SO}_4$ (Govoni & Nathanson 1994). Recent measurements by the space-based observatories ISO and SWAS are placing stringent abundance constraints on $\text{CO}_2$, $\text{H}_2\text{O}$ and $\text{O}_2$. Gaseous water is found to have high abundances in star-forming regions which are consistent with ice mantle evaporation or hydrogenation of atomic oxygen in shocked gas (Gensheimer, Maursberger & Wilson 1996; van Dishoeck & Hollme 1996; Harwit et al. 1998). In contrast, although water ice is ubiquitous along lines of sight towards dense molecular clouds, SWAS observations (Snell et al. 2000) indicate a gas abundance significantly below values expected from current steady-state chemical models. Bergin et al. (2000) developed a model in which the depletion of oxygen on to the surfaces of grains, as a result of the hydrogenation into water ice, perturbs the gas-phase chemistry to the point that the remaining gas-phase oxygen is taken up in carbon monoxide, with a small amount in atomic form and, with a much lower concentration, in $\text{O}_2$. In this case, $\text{H}_2\text{SO}_4$ would be only marginally hydrated.

Gas–grain cycling between clumps and the more diffuse interclump medium (Charnley et al. 1988, 2001) might change this conclusion. Recently, Goldsmith et al. (2002) reported the tentative detection of molecular oxygen emission in the $\rho$ Oph A cloud. The linewidth and the velocity are consistent with the redshifted wing emission by species that trace the molecular outflows seen in this region. The $\text{O}_2$/H$_2$ ratio in this high-velocity gas is approximately $10^{-3}$, much larger than the low abundances inferred from SWAS observations towards dense molecular clouds. Goldsmith et al. (2002) proposed a scenario that explains the low $\text{O}_2$ abundance in cloud cores along with the much enhanced abundance in the outflow region. The quiescent gas is impacted by a shock driven by an embedded young star (or stars). The critical assumption is the evaporation of water ice, which cycles oxygen back to the gas phase. During the warm phase the fractional abundance of gaseous water vapour increases significantly. At later times ($\gtrsim 10^5$ yr) in the cold post-shock gas, there is a steady build-up of water on grain surfaces as a result of direct freeze-out of $\text{H}_2\text{O}$ molecules and atomic oxygen hydrogenation to form water ice. In this phase, sulphuric acid might be efficiently hydrated.

### 3 OBSERVATIONAL DATA

Absorption spectra of interstellar ices from the Short Wavelength Spectrometer (SWS) on ISO towards two obscured young stellar objects, NGC 7538: IRS9 (Whittet et al. 1996; Schutte et al. 1996) and RAFGL 7009S (d’Hendecourt et al. 1996), can be interpreted to
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Figure 1. (a) Synthesized laboratory spectrum of H$_2$SO$_4 \cdot$ H$_2$O. The absorption coefficient is the sum of 18 Gaussian components. (b) Synthesized spectrum using the absorption coefficient from above. The flux (Jy) is that of a 700-K blackbody reduced by one power in frequency owing to scattering. The dotted line represents a fit to the interstellar spectrum of NGC 7538: IRS9 (Whittet et al. 1996).

provide support for the hypothesis that H$_2$SO$_4 \cdot$ nH$_2$O is an important repository of depleted sulphur. In order to simulate the interstellar spectra, we synthesize the absorption coefficient of mono-hydrated sulphuric acid H$_2$SO$_4 \cdot$ H$_2$O (Zhang et al. 1993) by the sum of 18 Gaussian features shown in Fig. 1(a). In Fig. 1(b) the interstellar spectrum of NGC 7538: IRS9 is superimposed to a synthesized spectrum derived using the absorption coefficient of H$_2$SO$_4$ and the

Table 1 reports the wavelength in µm and wavenumber in cm$^{-1}$ of the major bands of both the interstellar and laboratory spectra.

Of particular interest are the interstellar bands at 6.0 and 9.7 µm which are attributed to H$_2$O and silicates, respectively. The 6.0-µm feature is too broad to be entirely due to H$_2$O and contains some extra red and blue absorption (Schutte et al. 1996). The red excess is centred at 6.25 µm and is matched by the 6.19-µm feature in the spectrum of H$_2$SO$_4 \cdot$ nH$_2$O, with the stronger component in mono-hydrated sulphuric acid (Zhang et al. 1993). The broad silicate features seen in both interstellar spectra match and may obscure the absorption exhibited by H$_2$SO$_4$ in the 8.0–10.5 µm region. The absorption feature widens and weakens with an increasing number of bound water molecules (Zhang et al. 1993).

The 6.8-µm feature is currently unidentified, but magnesium carbonate MgCO$_3$ has been proposed (Sandford & Walker 1985; Hect et al. 1986). Magnesium carbonate should have an additional feature near 11.6 µm, which may be the obscured part of the strong extremely broad 9.7-µm band of silicates (Whittet et al. 1996).

The band at 4.67 µm attributed to CO has a corresponding feature in the spectrum of solid H$_2$SO$_4 \cdot$ nH$_2$O and the 3.0-µm band attributed to solid H$_2$O is also present in the spectra of crystalline hydrates of sulphuric acid. The centroid of the feature in hydrated sulphuric acid shifts to the red with increasing number of bound water molecules (Zhang et al. 1993).

In the two SWS/ISO spectra four features are present, at 3.0, 4.67, 6.0 and 9.7 µm, that have counterparts in the laboratory spectra of hydrated sulphuric acid, and the intensities of the interstellar bands correlate well with the intensities of the laboratory bands (Zhang et al. 1993). Thus sulphuric acid with incorporated water may be a component of dust together with the other species that are currently assigned. H$_2$SO$_4 \cdot$ nH$_2$O may account for an important part of the depleted sulphur.

4 HOT CORES

Hot molecular cores are believed to represent the earliest steps of massive stellar birth (Walmsley 1992). Hot cores are composed of hot (~100–300 K), dense (~10$^7$ cm$^{-3}$) gas and warm dust. Chemically, hot cores are characterized by high abundances of fully

<table>
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<tr>
<th>NGC 7538: IRS9</th>
<th>RAFGL 7009S</th>
<th>Assignment$^a$</th>
<th>H$_2$SO$_4 \cdot$ nH$_2$O$^b$</th>
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<tr>
<td>15.3</td>
<td>15.2 (657.9)</td>
<td>CO$_2$</td>
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<td></td>
<td>13.0 (769.2)</td>
<td>H$_2$O</td>
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<tr>
<td>9.7</td>
<td>9.7 (1030.9)</td>
<td>Silicates</td>
<td>8.0 (1250.0) – 10.5 (952.4)</td>
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<td>7.67</td>
<td>7.7 (1299.9)</td>
<td>CH$_4$</td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>6.85 (1459.8)</td>
<td>MgCO$_3$?</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>6.0 (1666.7)</td>
<td>H$_2$O</td>
<td>6.19 (1615.5)</td>
</tr>
<tr>
<td>4.67</td>
<td>4.67 (2141.3)</td>
<td>CO</td>
<td>4.42 (2262.4) – 4.76 (2100.8)</td>
</tr>
<tr>
<td>4.27</td>
<td>4.27 (2341.9)</td>
<td>CO$_2$</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>3.5 (3333.3)</td>
<td>CH$_3$OH</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>3.0$^c$ (3333.3)</td>
<td>H$_2$O</td>
<td>2.56 (3906.2) – 4.0 (2500.0)</td>
</tr>
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</table>

$^a$Whittet et al. (1996); Schutte et al. (1996); d'Hendecourt et al. (1996).

$^b$Zhang et al. (1993).

$^c$This band is totally saturated.
of hydrogenated molecules such as water, ammonia and hydrogen sulphide, along with a rich variety of complex organics. Such a chemical richness is explained by removal of molecular ice mantles from dust grains owing to evaporation above \( \sim 90 \) K, followed by rapid gas-phase ion–molecule reactions. The interaction of the outflows with the envelope produces shocks that can also remove molecular ice from mantles, and drive a high-temperature gas chemistry, involving both ion–molecule and neutral–neutral reactions (Charnley 1997). Hot cores are probably present even in low-mass protostars (Schöier et al. 2002).

Minh et al. (1990) detected large abundances of \( \text{H}_2\text{S} \) towards OMC-1 and also in several other star-forming regions. Large abundances of hydrogen sulphotide were also observed in the Orion Plateau source (Minh et al. 1991), where shock chemistry is believed to be important. Ion–molecule gas-phase formation of \( \text{H}_2\text{S} \) is inefficient in hot cores. Although alternative scenarios have been proposed (Minh et al. 1990), the presence of a saturated molecule in a hot core, at an abundance \( 10^2\)-\( 10^4 \) times its cold-cloud value, is very strong evidence for a grain surface origin. Erosion of molecular sulphotidated ices could deposit \( \text{H}_2\text{S} \) directly in the gas as a result of the fragmentation and hydrogenation of \( \text{H}_2\text{SO}_4 \cdot \text{nH}_2\text{O} \). In fact, sulphuric acid has not been detected in the gas phase (Hollis et al. 1981), and its hydrogenation to \( \text{H}_2\text{S} \) is thermodynamically allowed. Other species that are likely to be produced from hydrated sulphuric acid by destruction in hot regions are \( \text{OH}, \text{H}_2\text{O}, \text{SO} \) and \( \text{SO}_2 \).

In standard hot-core chemical schemes (Charnley 1997) the abundances of sulphur-bearing molecules like \( \text{SO}, \text{SO}_2, \text{OCS} \) and \( \text{H}_2\text{CS} \) are predicted to be drastically enhanced by the injection of \( \text{H}_2\text{S} \) into the hot-core region. Typically, these species are assumed to be second-generation products. Their abundances ratios can be used to determine the time elapsed since the evaporation of ice mantles has begun (Charnley 1997).

Based on observations of the deeply embedded young stellar object IRAS 16293 – 2422, Schöier et al. (2002) have discussed the possibility of very different chemical time-scales between low-mass and high-mass hot cores. During the formation of a low-mass star, the transit time for grains and molecules through the warm and dense region surrounding the protostar might be extremely fast (\( \sim \) a few hundred years). In this case, there would be no enough time for an extensive secondary chemistry to develop (cf. Charnley 1997). Thus the presence of \( \text{SO} \) and \( \text{SO}_2 \) with abundances comparable to that of \( \text{H}_2\text{S} \) in IRAS 16293 – 2422 (Schöier et al. 2002) might trace the chemical complexity derived from previous stages of grain mantles and gas-phase chemistry. If \( \text{H}_2\text{SO}_4 \cdot \text{nH}_2\text{O} \) is actually a component of interstellar ices, its release from grain surfaces could explain the high \( \text{SO}_2 \cdot \text{H}_2\text{O} \) ratios derived towards the young hot core IRAS 16293 – 2422 by Schöier et al. (2002).

5 CONCLUSIONS

The coincidence of features seen in SWS/ISO spectra with laboratory infrared spectra supports the suggestion that \( \text{H}_2\text{SO}_4 \) is formed on grains in collapsing clumps and may remove water from the gas phase by further hydrate formation to \( \text{H}_2\text{SO}_4 \cdot \text{nH}_2\text{O} \). Sulphuric acid might be the repository of all the depleted elemental sulphur in dense molecular clouds. Assuming a cosmic \( \text{O}/\text{S} \) ratio of approximately 50 (Snow & Witt 1996), mono-hydrated sulphuric acid would also represent \( \sim 10 \) per cent of the depleted oxygen. Products of thermal release of hydrated sulphuric acid might be present in the spectra of very young low-mass hot cores, with abundance ratios significantly different from those observed in higher mass, more evolved objects. Cosmic abundance considerations based on the inventory of the chemical content of the protostellar environment IRAS 16293 – 2422 (Schöier et al. 2002) show that a fraction of sulphuric acid might be released intact from grain surfaces. Chemical destruction processes act on time-scales much longer than the supposed lifetime of the region. If the early-time chemical scenario for the hot core surrounding IRAS 16293 – 2422 were confirmed, very young low-mass hot cores would provide a suitable environment in which \( \text{H}_2\text{SO}_4 \) emission might be detected.

Recently, Keller et al. (2002) discovered iron sulphide emission from discs surrounding two young stars. Our suggestion of the production of hydrated sulphuric acid during the collapsing phase may provide a link with the diffuse interstellar medium, where sulphur is usually not strongly depleted (Snow & Witt 1996), and evolved young star environments, where \( \text{FeS} \) has been detected. Retting & Brittain (2002) report the detection of the ro-vibrational bands of \( \text{CO} \) from the circumstellar material around a number of pre-main-sequence stars, including AB Aurigae, one of the two Herbig stars in which \( \text{FeS} \) emission has been detected (Keller et al. 2002). \( \text{CO} \) emission shows evidence that warm gas exists in the inner 50 au of the disc. Thus the formation of \( \text{FeS} \) may occur subsequently to the hot-core phase and may proceed by channelling products from thermally released \( \text{H}_2\text{SO}_4 \).

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