

Organosulfur Chemistry in Cometary Materials: Insights from ROSINA Data and Laboratory Simulations

Ahmed Mahjoub^{1,2}, Kathrin Altwegg³, Michael J. Poston⁴, Martin Rubin³, Robert Hodyss¹, Mathieu N. Choukroun¹, Bethany L. Ehlmann⁵, Nora Hanni³, Michael E. Brown⁵, Jordana Blacksborg¹, John M. Eiler⁵, Kevin P. Hand¹

¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California ²Space Science Institute, 4765 Walnut St, Suite B, Boulder, CO 80301, ³Physikalisches Institut, University of Bern, Bern, Switzerland, ⁴SWRI, San Antonio, Texas, ⁵Division of Planetary and Space Sciences, Caltech, Pasadena, 91010

Introduction: Growing evidence suggests that H₂S was a highly abundant molecule in the presolar nebula. One important question is the effect of H₂S on the composition and spectroscopy of organic heteropolymers, called tholins, that are believed to exist on the surfaces of small icy bodies, including comets and KBOs. Despite the importance of H₂S and the potential of sulfur chemistry to considerably affect the chemical reactivity in mixed ices, little has been published exploring this chemistry. We recently studied the role that H₂S could play in the chemistry [1,2], spectroscopy [3,4] and astrobiology [5] of small icy bodies - particularly KBOs and Jupiter Trojans. Here, we are discussing data from ROSINA measurements during the dust event showing the detection of large organosulfur molecules with low volatility embedded in the dust grains in comet 67P. We report also mid-infrared spectra of laboratory simulations of organic refractory materials produced by irradiation of simple ice mixtures with and without H₂S. This laboratory work shows a domination of sulfur chemistry when H₂S is added and points toward an ice chemistry origin of the rich sulfur-bearing species detected in the cometary material.

Laboratory simulations: Two residue samples were produced by irradiation of ice films under vacuum at 50 K. A tholin film “without sulfur” was produced from a starting ice of CH₃OH:NH₃:H₂O (3:3:1), and a tholin film “with sulfur” was produced from a starting ice mixture of CH₃OH:NH₃:H₂S:H₂O (3:3:3:1). Electron irradiation experiments were carried out using the Icy Worlds Simulation laboratory. The experimental setup consists of a high-vacuum stainless steel chamber pumped by a Varian Turbo and backed by oil-free pumps. The ices were vapor-deposited on a substrate attached to the cold finger of a closed-cycle helium cryostat. High-energy electrons (10 keV) were directed at the ice with a typical beam current of 0.5 μ A. All studied ices were submitted to the same fluence of electron energy $\sim 2 \times 10^{21}$ eV cm⁻². After irradiation for 19 hours at 50 K, samples were warmed to 120 K at 0.5 K minute⁻¹ and held there for 1 additional hour under continued electron irradiation. After the electron irradiation was concluded, the samples were warmed at 0.5 K minute⁻¹ to 300 K. The resulting residue films were characterized at room temperature using a Midac FTIR spectrometer.

Results and discussions: Figure 1 shows a comparison between the infrared spectra of “with sulfur” and “without sulfur” residues.

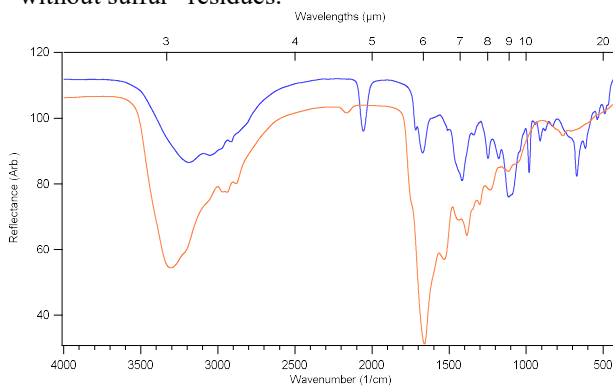


Figure 1: Infrared spectra of: “with sulfur” residue sample (blue) and “without sulfur” sample (orange)

Comparison between infrared spectra shows a clear difference over the entire spectrum, suggesting a dramatic change of the chemical composition of the residue when H₂S is added. The strong NH and OH bands at 3200 and 3300 cm⁻¹ as well as the CN and CO bands around 1600 cm⁻¹ and 2200 cm⁻¹ were clearly decreased in the “with sulfur” sample compared to the “without sulfur” sample. The same decrease is also observed for bands around 3000 cm⁻¹ assigned to CH stretching modes. For example, the C=O absorption band at 1660 cm⁻¹ is 3 times deeper in the “without sulfur” sample while the broad band between 3000 and 3200 cm⁻¹ is 2 times deeper. This strongly indicates a depression of carbon, nitrogen and oxygen containing compounds in the residue when H₂S is added to the ice composition. A more pronounced difference between the two spectra is the strong band at 2057 cm⁻¹ in the “with sulfur” sample that is totally absent in the “without sulfur” sample. This band is correlated to sulfur and could be tentatively assigned to the N=C=S group. At the finger print region, the “with sulfur” residue displays strong new bands between 500 and 700 cm⁻¹ and between 1000 and 1500 cm⁻¹. These absorption features are assigned to sulfur containing CS, SO and SS vibrational modes. The vibrational modes CS and SS usually result in weak absorption bands below 900 cm⁻¹. The observed bands in the spectrum of the “with sulfur” sample suggest that molecules/functional groups rich in CxSyHzOw moieties dominate the composition of the residue when H₂S is added to the starting ice film.

These results show that the effect of H_2S on the refractory residue is important and should be considered in the characterization of tholins in small icy bodies and interstellar icy grains.

Figure 2 shows a comparison between the infrared spectrum of “with sulfur” residue and the spectrum of comet 67P averaged from VIRTIS-M spectra between August and September 2014. This spectral range contains contributions from OH, NH and CH chemical groups.

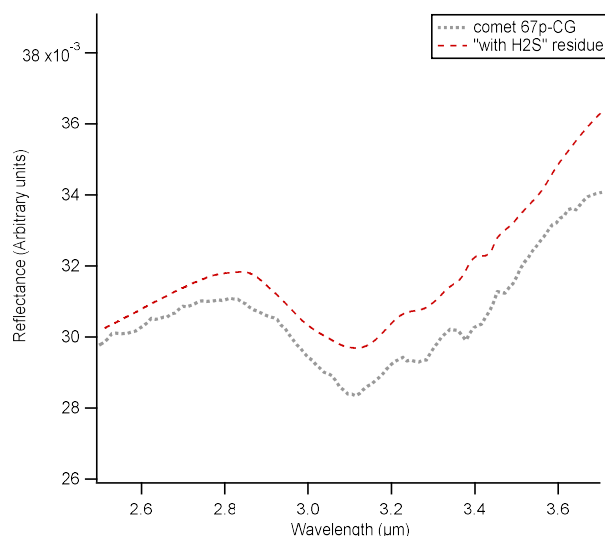


Figure 2: comparison between the infrared spectrum of “with sulfur” tholin sample and the VIRTIS averaged spectrum of comet 67P [6]

The two spectra display very similar bands at 3.1 and 3.25 μm . In addition, the two spectra show a similar slight shoulder at 3.0 μm . This shoulder is probably due to OH stretching modes. Variations of the depth of this band have been observed during the *Rosetta* mission and they have been correlated to variation of contribution from water ice. The band at 3.1 μm has been assigned to the NH_4^+ cation in ammonium salts [7] but it could also be due to other NH and NH_2 groups of organics tholins produced by irradiation of ice films as shown in figure 2. The structures of bands in the spectrum of 67P-CG around 3.4 μm could be assigned unambiguously to carbon-hydrogen CH chemical groups and correspondingly to different hybridizations (sp^2 , sp^3 and sp) of carbon atoms.

ROSINA measurements of sulfur rich organics:

ROSINA measurements of dust particles, during the dust storm event on September 5th 2016 [8], show the detection of large organosulfur molecules and the increase of abundances of sulfurous molecules previously detected in the coma. The ROSINA data support the presence of sulfur bearing non-volatile organics on the surface of comet 67P. The S/O ratio estimated during the dust event is one order of magnitude higher than the ratio of the undisturbed

coma, indicating that the gas phase accounts only for a small fraction of the total elemental sulfur composition of the comet materials.

In addition to the species already detected in the undisturbed coma, a plethora of other sulfurous species are first-time detected during the dust event. These are mainly heavy molecules (or fragments due to dissociation of larger molecules) that are not volatile enough to be detected in the gas phase and their detectability enhanced in dust event. Indeed, during the dust event particles entered the ion source at temperature $T = 273$ K. Semi-volatile molecules sublimated slowly over the course of many hours at this temperature.

Conclusion and perspectives:

The main finding of this work is the detection of large sulfur-bearing molecules of low volatility in dust grains of the comet 67P. Our laboratory simulation suggests that organo-sulfur molecules are effectively produced in the ice mixture “with sulfur” $\text{CH}_3\text{OH}:\text{NH}_3:\text{H}_2\text{S}:\text{H}_2\text{O}$, indicative of a plausible origin of sulfur compounds detected by ROSINA. Considering the remarkable difference between the infrared spectra of “with sulfur” and “without sulfur” at wavelengths longer than 5 μm , we will discuss the possibility of using the James Webb Space Telescope (JWST) to characterize the presence of organosulfur materials in different comets and other small icy bodies of the solar system.

Acknowledgments: This work has been supported in part by the NASA/RDAP program and by the Keck Institute for Space Studies (KISS). Part of this work was supported by NASA/DDAP program under grant number 80NSSC21K1015. This work has been conducted at the JPL, Caltech, under a contract with the National Aeronautics and Space Administration (NASA) and at the Caltech Division of Geological and Planetary Sciences. ROSINA would not have produced such outstanding results without the work of the many engineers, technicians and scientists involved in the mission, in the Rosetta spacecraft team and in the ROSINA instrument team over the past 20 years, whose contributions are gratefully acknowledged. Rosetta is an ESA mission with contributions from its member states and NASA. We acknowledge herewith the work of the whole ESA Rosetta team.

References:

- [1] Mahjoub A. et al. (2016) *ApJ* 820, 141. [2] Mahjoub A. et al. (2017) *ApJ* 846, 148. [3] Poston M. et al. (2018) *ApJ* 856, 124. [4] Mahjoub A. et al. (2021) *ApJL*, 914, L31. [5] Mahjoub A. and Hodyss (2018) *ApJ*, 869, 98. [6] Raponi A. et al. (2020) *Nature Astronomy* 4, 500-505. [7] Poch O. et al. (2020) *Science*, 367, eaaw7462. [8] Atwegg K., et al. (2017) *MNRS*, 469, 2, S130-S141