

An infrared measurement of chemical desorption from interstellar ice analogues

Y. Oba^{1*}, T. Tomaru¹, T. Lamberts², A. Kouchi¹ and N. Watanabe¹

¹Institute of Low Temperature Science, Hokkaido University, Sapporo, Hokkaido, Japan. ²Institute for Theoretical Chemistry, University of Stuttgart, Stuttgart, Germany. *e-mail: oba@lowtem.hokudai.ac.jp

Jyotirmoy Ghosh 06-08-18 ¹

In the background



Desorption is an important process which allows the migration of different species (which originate on the dust particle) to molecular clouds or gas phase.



Fig. 4. Illustration of the chemical desorption process. After an initial meeting (1), the molecule is highly excited; (2) and converts a fraction of its energy into vertical motion through interaction with the surface (3).

Relevance of this work

- ➢ The presence of several chemical species in molecular clouds that cannot form efficiently in the gas phase can occur only on interstellar dust.
- However, the specific mechanism that allows the formed species on the surface to populate the gas phase is still unknown.
- It appears that many reactions occurring on dust grains are accompanied with an excess energy which is too large to dissipate. Consequently, the formed species are ejected in the gas phase upon formation. This process, called chemical desorption is one of the answer to it.
- The chemical desorption process is more efficient process than other desorption process.

In this paper

- Astronomical observations have detected over 150 different species in the gas phase in these clouds. Migration mechanism of these species to the gas phase is crucial for understanding the chemical evolution in such cold clouds.
- > The first infrared in situ measurement of chemical desorption during the reactions of H_2S is reported, which are key to interstellar sulphur chemistry.
- The effective cross-sections for the chemical desorption of H₂S are determined by in situ infrared and TPD measurements.
- > The present study clearly demonstrates that chemical desorption is a more efficient process for releasing H_2S into the gas phase than was previously believed.
- The obtained effective cross-section for chemical desorption indicates that the chemical desorption rate exceeds the photodesorption rate in typical interstellar environments.

H atoms



$H + H_2S \rightarrow HS + H_2$ (reaction 1)

 $HS + H \rightarrow H_2S$ (reaction 2)

Exothermic reaction



Fig. 1 | **FTIR spectra of samples. a**, Solid H_2S (~0.7 monolayer) deposited on ASW (~30 monolayers). The inset shows an enlarged spectrum focusing on the S-H stretching band of H_2S (2,570 cm⁻¹)¹⁸. **b**, Difference spectra after exposure to H atoms for 20 (top), 60 (middle) and 120 min (bottom). The spectral change at around 2,300 cm⁻¹ is due to the temporal variation of atmospheric CO₂ concentration in the infrared beam line outside the vacuum chamber.



Fig. 2 | Variations in the relative abundance of solid H₂S on ASW with relevance to H atom exposure times. The solid line is a single exponential fit to equation (1) (see Methods). Each data point is an average of three measurements, with the s.d. of the mean values indicated by the error bars.

 $\Delta[\mathrm{H}_{2}\mathrm{S}]_{t}/[\mathrm{H}_{2}\mathrm{S}]_{0} = A(1 - \exp(-\sigma\phi t))$ eqn. 1

where $\Delta [H_2S]_t$, A, σ and ϕ represent the variation in the abundance of H_2S at time t, a saturation value for the desorption fraction of H_2S , the effective cross-section of chemical desorption in cm² and the flux of H atoms (~1.3 × 10¹⁴ atoms cm⁻²s⁻¹), respectively. By fitting the plots in Fig. 2 into equation (1), we obtain $\sigma = 2.2 \times 10^{-17}$ cm² for the chemical desorption of H_2S from ASW.



Supplementary Figure 1. Variations in the relative abundance of H_2S after exposure to H atoms on ASW (black solid squares) and on crystalline H_2O ice (red open circles). The desorption fraction is larger for the reaction on crystalline ice (~80% of the initial H_2S) than on ASW (~60%). Solid lines are guides for the eyes. Each data point is an average of three measurements with the standard deviation of the mean value.



Fig. 3 | TPD spectra. Solid H_2S (m/z = 34) from ASW obtained after exposure to H atoms (solid red line) and H_2 molecules without H atoms (H-blank experiment; dashed black line).

Isotope labelling experiments

 $H_2S + D \rightarrow HS + HD$ (R3)

 $HS + D \rightarrow HDS$ (R4)

 $HDS + D \rightarrow DS + HD$ (R5)

 $DS + D \rightarrow D_2S$ (R6)



Fig. 4 | Difference spectra of solid H₂S after exposure to D atoms for varying lengths of time on ASW. Top: 5 min. Middle: 10 min. Bottom: 30 min. The S-D stretching band of deuterated sulphides was observed at ~1,860 cm⁻¹. The spectral change at around 2,300 cm⁻¹ is due to the temporal variation of the atmospheric CO₂ concentration in the infrared beam line outside the vacuum chamber.



Supplementary Figure 3. Variations in the relative abundance of solid D_2S after exposure to D atoms on amorphous D_2O ice for 120 min (blue solid triangles). Those of solid H_2S after exposure to H atoms (black solid squares) are also shown for comparison. The solid lines are guides for the eyes. Each data point is an average of three measurements with the standard deviation of the mean value.



