Hydrogen sulfide clathrate hydrate FTIR spectroscopy: A help gas for clathrate formation in the Solar System?

E. Dartois [a,*,1], Ph. Duret [a], U. Marboeuf [b], B. Schmitt [b]

[a] Institut d'Astrophysique Spatiale, UMR-8617, Université Paris-Sud/CNRS–INSU, bâtiment 121, 91405 Orsay, France
[b] Institut de Planétologie et d'Astrophysique de Grenoble, UMR-5274, UJF-Grenoble 1/CNRS–INSU, Grenoble F-38041, France

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ABSTRACT

Clathrate hydrates may affect the stability and evolution of volatile species in comets and planets. Among abundant volatiles species, hydrogen sulfide forms one of the most stable clathrate hydrate and may play a major role in the initiation of the clathration process, as well as significantly affect the fraction of each volatiles species encaged in the clathrate structure with respect to the initial gaseous reservoir. In this study we investigate the hydrogen sulfide clathrate hydrate infrared signatures. Several pure and co-mixed hydrogen sulfide clathrate hydrates are produced and analyzed by infrared spectroscopy. The H_2S clathrate hydrate specific vibrational transitions are recorded for an potential future search in planetary science and astrophysics, and its role as a clathrate hydrate promoter addressed.

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1. Introduction

Hydrogen sulfide is one of the most important sulfur bearing molecule believed to be present in the early Solar System. H_2S is also the most abundant sulfur molecule observed in comets coma (e.g. Crovisier, 2006). Besides its lower abundance as compared to other molecules such as methane or carbon dioxide in some atmospheres, its much higher stability with respect to the formation of a clathrate deserves further investigation. Following the expected thermodynamic path of the cooling solar nebula, it is predicted as the first potential clathrate to form (e.g. Iro et al., 2003; Mousis et al., 2010), provided that there is enough water available for enclathration, and that kinetics allow for the formation of clathrates when the temperature crosses the stability curve in the considered feeding zones, i.e. at low pressure (10^{-7} bars of H_2 or about 10^{-11} partial pressure bars of H_2S) and low temperature (about 80 K), during the cooling of the solar nebula. In addition, the presence of H_2S in comets could promote the formation of this structure of ice as it increases the stability of the corresponding mixed guest clathrate formed (e.g. Marboeuf et al., 2011a).

In this article we search the conditions of detection of the H_2S clathrate hydrate in astrophysical environments by mixing this molecule with others volatile molecules mainly of astrophysical interest, but not only. We investigate the infrared spectrum of the pure H_2S clathrate hydrate and co-mixtures with other molecules, to identify their different cages specific signatures, for a future comparison to remote spectra of Solar System objects. We experimentally show how the competition with other hydrate formers favors the clathrate hydrate cages filling by the hydrogen sulfide guest in most cases. As a consequence, even at low fractional abundance, H_2S can act as a stabiliser in clathrate hydrate cages formation. In Section 2 we first describe the experiments, followed in Section 3 by the results. A discussion of the implications for clathrate hydrate formation concerning hydrogen sulfide in particular and sulfur bearing molecules in general is given in Section 4, just before concluding remarks in Section 5.

2. Experiments

H_2S was purchased from Air liquide. The initial purity is N25 (99.5%) and main contaminants are OCS and CS_2 at a level of less than 2000 ppm. For the pure H_2S clathrate, the gas was distillated by sublimation. In mixtures, it was used as received. D_2S (97%D) was bought from Sigma–Aldrich and used as received. The other gases were also from air liquide and of higher level of purities.

A gold coated copper cell is thermally coupled to a liquid He-transfer cold finger, placed in an high-vacuum, evacuated cryostat ($P < 10^{-7}$ mbar). Two millimeter thick infrared transmitting zinc selenide windows are sealed with indium gaskets, and allow the spectrometer beam to record the clathrate hydrate spectra. A soldered stainless steel injection tube, brazed to the lower part of

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the cell allows for the entrance of gas or its evacuation. A description of the cell can be found in e.g. Dartois et al. (2010).

To prepare the clathrate, vapor water is injected in the evacuated cell precooled to 240 K, and condenses on the ZnSe windows (2 mm thick). The guest gases are then injected, with a predefined molar abundance ratio, in large pressure excess (see Table 1, often more than 10 times the expected equilibrium pressure at the given temperatures). The cell is subsequently maintained in this state during 12 h and up to 3 days to ensure proper clathration. After this long exposure of the water ice to high pressure of the guests, the clathrate is formed and the cell temperature is lowered while the excess gas pressure is evacuated. The cell is maintained at a pressure and temperature above the estimated clathrate stability curve until about 140 K, where the gas is evacuated (final $P \leqslant 10^{-7}$ mbar) while pursuing the temperature descent to its minimum. This 140 K temperature is chosen because the kinetics at these temperatures are slow enough that the clathrate hydrate is stable during the depressurization and high enough to evacuate the possible condensates of the guest gases at high pressure or ice layers formed by remaining impurities naturally present in H_2S. Infrared spectra are therefore recorded in the 7000–650 cm^{-1} range, raising the temperature step by step from its minimum. The recording of each spectrum typically lasts one hour and the temperature is raised at 1–2 K/min in between each temperature step. Spectra are recorded until the declathration is observed (first as a slight increase in the background pressure above the 10^{-6} mbar range, measured dynamically while evacuating). Once the dynamical pressure increases, we know that the sample is evolving. The measurements are therefore considered as no longer reliable when kinetics effects declathrate the sample on timescales of the order of or lower than the measurement timescale. This is what fixes the upper limit at which the temperature steps are valid. The sensitivity at which we start to detect the pressure increase is such that the number of molecules flowing out of the sample is still low as compared to the thickness of the sample.

In the very first experiments conducted, we faced problems in efficiently removing pure hydrogen sulfide that condensed on the clathrate, due to insufficient waiting time for the pressure to drop below the desired pressure limit before starting the temperature descent, as we were concerned about a premature declathration of the sample formed. As a consequence some residual H_2S gas used to apply the pressure remains trapped in the cell, giving rise at low temperatures to a small triple band contribution in the spectrum, typical of the phase III H_2S solid for the condensed pure phase or in interaction at the surface of the ice network. To remove these contributions and make sure that only the clathrate phase remain we had in particular to significantly raise the temperature under vacuum, to efficiently evacuate the residual H_2S gas condensation or adsorption on the clathrate ice network.

In order to confirm the structure in which H_2S condenses, a mixture of H_2S and carbon dioxide was employed to form a mixed clathrate. The position of the observed CO_2 antisymmetric absorptions at 2337 cm^{-1} and 2347 cm^{-1} clearly point out to a type I structure (Fleyfel and Devlin, 1988; Dartois and Schmitt, 2009), shown in the co-mixed spectra figure. Individual peak intensities are different from the pure CO_2 clathrate due to cage filling factors strongly favoring the large cage CO_2 occupancy in the H_2S/CO_2 clathrate, keeping in mind that the overall cages filling of both small and large cages is still dominated by the H_2S species. Pure H_2S and D_2S clathrate hydrate were measured. Several co-mixed H_2S/X mixtures (X = CO_2, C_2H_6, Xe, C_3H_8, iso-C_4H_{10}, SF_6) were produced, in order to study the expected variations in the clathrate small and large cages occupancies. A summary of the experiments is given in Table 1. Pure H_2S hydrate is expected to form the structure I clathrate hydrate (CLH), with two small water-molecule pentagonal dodecahedron cages (S = 5^{12}) and six large hexagonal truncated trapezohedron cages ($L_I = 5^{12}6^2$) in the unit cell, with the general formula ($2S \cdot 6L_I \cdot 46H_2O$). When co-mixed with CO_2, C_2H_6 or Xe, we observe that the structure I is also formed. With large molecules such as propane (C_3H_8), isobutane (i-C_4H_{10}) or sulfur hexafluoride (SF_6), a structure II is produced, in which the large cage is a ($L_{II} = 5^{12}6^4$), with the general formula ($16S \cdot 8L_{II} \cdot 136H_2O$). C_3H_8, i-C_4H_{10} and SF_6 enter only in the large cages. A schematic view on the corresponding clathrate types is given in Fig. 1. Classical FT-IR post treatment was performed to extract the spectra presented in this article, i.e. local polynomial baseline corrections as well as frequency filtering to eliminate the high frequency fringes residuals of the interfering beams arising from multiple reflections between both surfaces of our well polished cell windows. The temperature dependent infrared spectra of the various investigated hydrogen sulfide, deuterium sulfide and co-mixted clathrates are displayed in Figs. 2–4, respectively. In the case of the D_2S clathrate, hydrogen exchange during the pressurization with the remaining water vapor converted some of the D_2S molecules to HDS, and the clathrate produced is a mixture of both, as seen from the stretching modes corresponding to the HS and DS bonds in the HDS molecule. The clathrate is still largely dominated by D_2S. In the case of the Xe:H_2S clathrate hydrate with the lowest Xe concentration, only the low temperature spectra could be recorded due to signal to noise limitations.

Table 1
Summary of clathrate hydrate experiments[a] and modeling.

Guest	H_2S Partial P. (bars[b])	P. total (bars)	Struct.	η^{X}[c] Meas. ($\pm 3\sigma$)	η^{X}[c] Calc.
H_2S	7.0	7	I	1.0 ± 0.08[d]	1.02
D_2S	∼7.0	7	I	n.a.	n.a.
Co-mixtures (X/H_2S)					
CO_2	0.5	4	I	0.82 ± 0.09	0.77
C_2H_6	0.9	11	I	0.89 ± 0.02	0.24
Xe	0.4	3.4	I	0.83 ± 0.06	0.74
OCS	0.4	4	I	0.47 ± 0.09	–
Xe	0.025	3	I	0.62 ± 0.12	0.68
C_3H_8	0.4	3.0	II	$\leqslant 0.06$	0.01
iso-C_4H_{10}	1.7	3.2	II	$\leqslant 0.03$	0.003
SF_6	0.4	3.4	II	$\leqslant 0.02$	0.001

[a] The formation temperature is 240 K in all experiments.
[b] D_2S for the perdeuterated experiment.
[c] $\eta^{X} = \left(\int L_I^X / \int S_I^X \right) / \left(\int L_I^{H_2S} / \int S_I^{H_2S} \right)$, measured at low temperature to increase the contrast. See text for details.
[d] By definition, corresponding to the ratio of cages filling.