



Thio residue from thermal processing of cometary ices containing carbon disulfide and ammonia

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Abstract

We have carried out experimental investigation on binary ice mixture containing carbon disulfide (CS₂) and ammonia (NH₃) ices formed at 10 K. Icy films were formed in various combinations to investigate the reactivity of CS₂ and NH₃ molecules on cometary nucleus. In the case of NH₃ ices, deposition carried out at 10 K was found to contain NH₃ homo-dimers that was found to reorient upon annealing to 40 K. Phase transition was found to take place as the 10 K ice was warmed to higher temperatures and the phase transition temperature was found to be 5 K higher for the mixed ice in comparison to the layered deposits. Thermal processing of the mixed deposition of CS₂–NH₃ ice was found to leave thio residue, which could be ammonium dithiocarbamate that was even found to be present at 340 K.

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1. Introduction

Comets are known to harbor variety of simple and complex molecules. Irradiation and thermal processing of simple ices present may lead to the formation of complex molecules (Flynn et al., 2006; McKeegan et al., 2006). In fact, the recent discoveries on the new simple and complex molecules (such as amide and polyoxymethane) on comets are added evidences (Wright et al., 2015). However, the formation of such molecules could be due to photolysis and/or thermal processing. In order to understand the role of molecules that are already known to be present on a cometary nucleus, laboratory simulations of cometary nucleus

are needed. Here we select two of the simple molecules, CS₂ and NH₃, that are known to be present on comets and such a mixture is studied in laboratory analogs.

First direct detection of CS₂ was made in 1995 in Comet 122P/de Vico by comparing the unidentified spectral lines of the comet in the visible and ultraviolet region with the experimental spectra of supersonically cooled CS₂ (Jackson et al., 2004). Perhaps this discovery was only after fifteen years since the first identification of C–S bonds in Comet West in 1980 (Smith et al., 1980). Recently (Sivaraman, 2016) the presence of CS₂ molecules on cold regions of Lunar south pole was confirmed. The first identification of NH₃ on a comet was made in the 1980's in Comet 1983 d (Altenhoff et al., 1983). It was estimated that six percent of the gases subliming from the nucleus of the comet were NH₃. Measurements using Gas Chromatography Mass

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Spectrometer (GCMS) onboard Huygens probe revealed the nitrogen rich atmosphere of Titan is in fact from the impact driven chemistry of NH_3 which is a major constituent in the upper and mid atmosphere of Titan (Niemann et al., 2005).

NH_3 and CS_2 molecules being widely present in many planetary bodies including comets, it is of utmost interest to the planetary scientists and therefore extensive spectroscopic studies have been done on these two molecules in astrophysical conditions (Fresneau et al., 2014; Garozzo et al., 2010; Maity and Kaiser, 2013; Mangum et al., 2013). Though these two molecules were investigated, however their reactivity in mixtures at low temperature are yet to be explored. Similar thermal reactivity of NH_3 and CO_2 were investigated in solid phase (Bossa et al., 2008a,b; Lv et al., 2014; Noble et al., 2014; Rodriguez-Lazcano et al., 2014) and have found to form ammonium carbamate and carbamic acid. Here we present the results of the thermal processing of the binary ice mixture containing CS_2 and NH_3 ices deposited in various combinations and probed using Fourier Transform InfraRed (FTIR) Spectroscopy, in astrophysical conditions.

2. Experimental method

Experiments were carried out in the new experimental chamber housed in the laboratory for low temperature astrochemistry at Physical Research Laboratory (PRL), India. An Ultrahigh Vacuum (UHV) chamber, that can reach base pressures up to 10^{-10} mbar, containing a cold head with Zinc Selenide (ZnSe) substrate cooled down to 10 K was used to simulate the cometary ices. An all metal leak valve was used to introduce gases to form molecular ices on to the cooled ZnSe substrate at 10 K.

CS_2 , 99.9% pure vapor (molecules), from the liquid sample were let into the chamber through after two freeze–pump–thaw cycles at liquid nitrogen temperature. NH_3 , 99.99% pure, were let into the chamber through the gas line. A gas mixing chamber was used to mix both the molecules before they were let into the chamber to condense on to the ZnSe substrate kept at 10 K. Molecular ices thus formed at 10 K was then warmed to higher temperatures and subsequently probed in the Mid-IR region ($4000\text{--}500\text{ cm}^{-1}$), resolution of 2 cm^{-1} , using Fourier Transform InfraRed (FTIR) Spectrometer.

After recording InfraRed (IR) spectra for pure samples experiments were performed with binary ice mixtures in different combinations:

(i) CS_2 molecules were let into the UHV chamber to form CS_2 ice on the ZnSe substrate at 10 K. Then NH_3 molecules were inlet into the chamber and were made to condense over the CS_2 molecular ice at 10 K. A spectrum was recorded at 10 K and the ice layers were warmed to higher temperatures with subsequent recording of spectra at different temperatures until sublimation.

(ii) NH_3 molecules were let into the UHV chamber to form NH_3 ice on the ZnSe substrate at 10 K. Then CS_2 molecules were inlet into the chamber and were made to condense over the NH_3 molecular ice at 10 K. A spectrum was recorded at 10 K and the ice layers were warmed to higher temperatures with subsequent recording of spectra at different temperatures until sublimation.

(iii) Both NH_3 and CS_2 were prepared in the gas mixing chamber before letting into the UHV chamber to form icy mixture of NH_3 and CS_2 on the ZnSe substrate kept at 10 K. A spectrum was recorded at 10 K and the ice mixture was warmed to higher temperatures with subsequent recording of spectra at different temperatures until sublimation.

3. Results and discussion

3.1. Pure CS_2 ice

Spectrum recorded after pure CS_2 deposition at 10 K revealed characteristic bands that correspond to CS_2 molecules in the $2500\text{--}1000\text{ cm}^{-1}$ region (Fig. 1(a)). The most intense peaks observed at 1525 cm^{-1} and 1460 cm^{-1} were assigned to C–S symmetric stretching. Few other bands with peak positions at 2145 cm^{-1} , 2106 cm^{-1} , 2214 cm^{-1} , 2284 cm^{-1} were assigned (Maity et al., 2013) to combination vibration modes as mentioned in Table 1. Upon warming the ice changes observed in the fundamental modes indicated a phase change from amorphous to crystalline to have completed at 80 K. Polycrystalline CS_2 is being reported to form when it is vapor deposited at 80 K (liquid nitrogen temperature) (Yamada and Person, 1964).

3.2. Pure NH_3 ice

Pure NH_3 molecules were deposited on the substrate and a spectrum was recorded at 10 K where several peaks were found to appear in the $3500\text{--}1000\text{ cm}^{-1}$ region (Fig. 1(b)). The bands at 3375 cm^{-1} , 3311 cm^{-1} , 3244 cm^{-1} and 3208 cm^{-1} were assigned to N–H symmetric stretching (Dows et al., 1955). The band at 1872 cm^{-1} , 1649 cm^{-1} and 1627 cm^{-1} are assigned to H–N–H scissoring vibrations. The most intense band at 1060 cm^{-1} is assigned to N–H wagging vibration. The spectral signatures confirmed (Fig. 2) phase change from amorphous to crystalline NH_3 (Zheng and Kaiser, 2007) to have occurred in the ice at 65 K. The two new bands with peak positions at 3311 cm^{-1} and 3244 cm^{-1} are attributed to the formation of homo-dimers that undergo reorientation upon annealing to higher temperatures. The bands at 3311 cm^{-1} and 3244 cm^{-1} were then found to be missing in the spectrum recorded at 40 K (Fig. 2). Rearrangement of such homo-dimers is known from earlier studies on molecules in the condensed phase (Sivaraman et al., 2012, 2013). Such a change happening within the ice formed at 10 K and

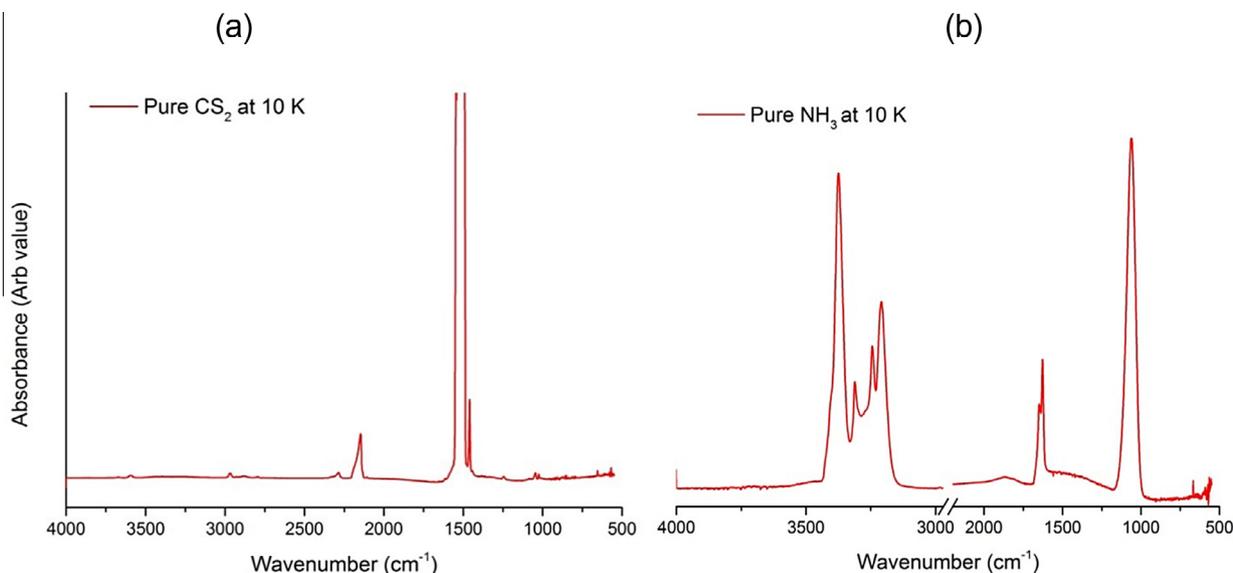


Fig. 1. Infrared spectra of (a) pure CS₂ at 10 K and (b) pure NH₃ at 10 K. Line break was introduced in (b) in order to enhance the spectral features in the 3500–3000 cm⁻¹ region.

Table 1
Peak positions and band assignments. Assignments for NH₃ and CS₂ are taken from Maity et al. (2013) and Zheng and Kaiser (2007), respectively.

NH ₃				CS ₂			
10 K	65 K	80 K	Band assignment	10 K	65 K	80 K	Band assignment
3375.6	3375	3375.2	v ₃ (N–H degenerated stretching)	2284.4	2284.4	2286.9	2v ₂ + v ₃ (combination band)
3311.0	3288.8	3288.8	v ₁ or 2v ₄ (N–H symmetric stretching)	2214.6	2216.4	2219.1	2v ₂ + v ₃ (combination band)
3244.7	–	–	v ₃ (N–H degenerated stretching)	2145.5	2145.3	2145.1	v ₁ + v ₃ (C–S stretching)
3208.7	3206.1	3206.1	v ₁ (N–H symmetric stretching)	2106.3	2105.7	2100.7	v ₁ + v ₃ (C–S stretching of ¹³ CS ₂)
1872.7	1895.1	1896.1	v ₄ + v _L (H–N–H Scissoring)	1516.1	1507	1508.1	v ₃ (C–S stretching)
1649.7	1645.7	1645.7	v ₄ (H–N–H Scissoring)	1460.8	1459.5	1455.9	v ₃ (C–S stretching of ¹³ CS ₂)
CS ₂ + NH ₃ – mixed deposit							
3377.8	3368.2	3377.8		2168.1	2154.1	2158.8	
3311.4	3292.9	3288.1		1520.5	1516.6	1516.7	
3244.2	–	–					
3207.9	3207.9	3205					
1868.5	1869.2	1869.2					
1649.9	1652.7	1652.7					
1627.3	1635.8	1635.8					
1058.8	1072.9	1095.5					

warmed to 40 K suggests that the ice formed at 10 K could be highly porous as it is rich in homo-dimers of NH₃.

3.3. CS₂ below NH₃

Layered deposition for CS₂ below NH₃ was carried out at 10 K and an IR spectrum was recorded. Characteristic vibrational signatures of NH₃ and CS₂ were found to be present in the spectra recorded at 10 K (Table 1). Icy layers thus formed were heated to higher temperatures with subsequent recording of IR spectra. From the temperature dependent IR spectra in Fig. 3(a) we find that the intensity of the bands gradually decreases when the sample is warmed to higher temperatures and both NH₃ and CS₂ ices sublime after 120 K. A phase change temperature from

amorphous to crystalline form was found to be 80 K for CS₂ and 65 K for NH₃.

3.4. NH₃ below CS₂

Layered deposition for NH₃ below CS₂ was carried out at 10 K and an IR spectrum was recorded. Characteristic vibrational signatures of CS₂ and NH₃ were found to be present in the spectra recorded at 10 K (Table 1). Icy layers thus formed were heated to higher temperatures with subsequent recording of IR spectra. From the temperature dependent IR spectra in Fig. 3(b) we find that the intensity of the N–H symmetric stretching bands at 3375 cm⁻¹, 3311 cm⁻¹, 3244 cm⁻¹ and 3208 cm⁻¹ is present till 130 K due to crystalline CS₂ on top of NH₃ which was resisting NH₃ sublimation. Thus the intensity of the N–H symmet-

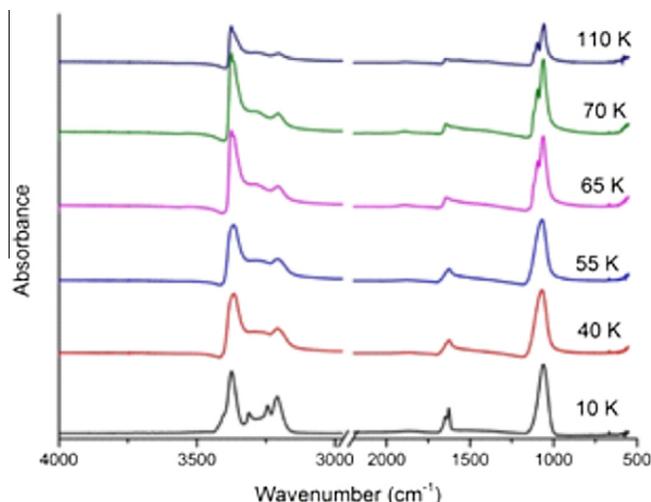


Fig. 2. Temperature dependent infrared spectra of pure NH_3 with the presence of homo-dimers at 10 K which got reoriented when warmed to 40 K.

ric stretching bands remains high till 130 K and then sublimation started while CS_2 molecules started to sublime. The phase change temperature from amorphous to crystalline form was found to be the same as in the case of CS_2 below NH_3 ; 80 K for CS_2 and 65 K for NH_3 .

3.5. Ice mixtures NH_3 , CS_2

Both NH_3 and CS_2 were mixed in the gas line and deposited at 10 K. An IR spectrum was recorded at 10 K. IR bands of NH_3 and CS_2 in Table 1 were found to be present in the spectra recorded at 10 K. The ice mixture was warmed to higher temperatures and a spectrum was recorded at until 340 K (Fig. 3(c)). Here again we find that the intensity of the N–H symmetric stretching bands at 3375 cm^{-1} , 3311 cm^{-1} , 3244 cm^{-1} and 3208 cm^{-1} is present till 110 K. The phase change was found to occur at a temperature which is 5 K higher than the phase change temper-

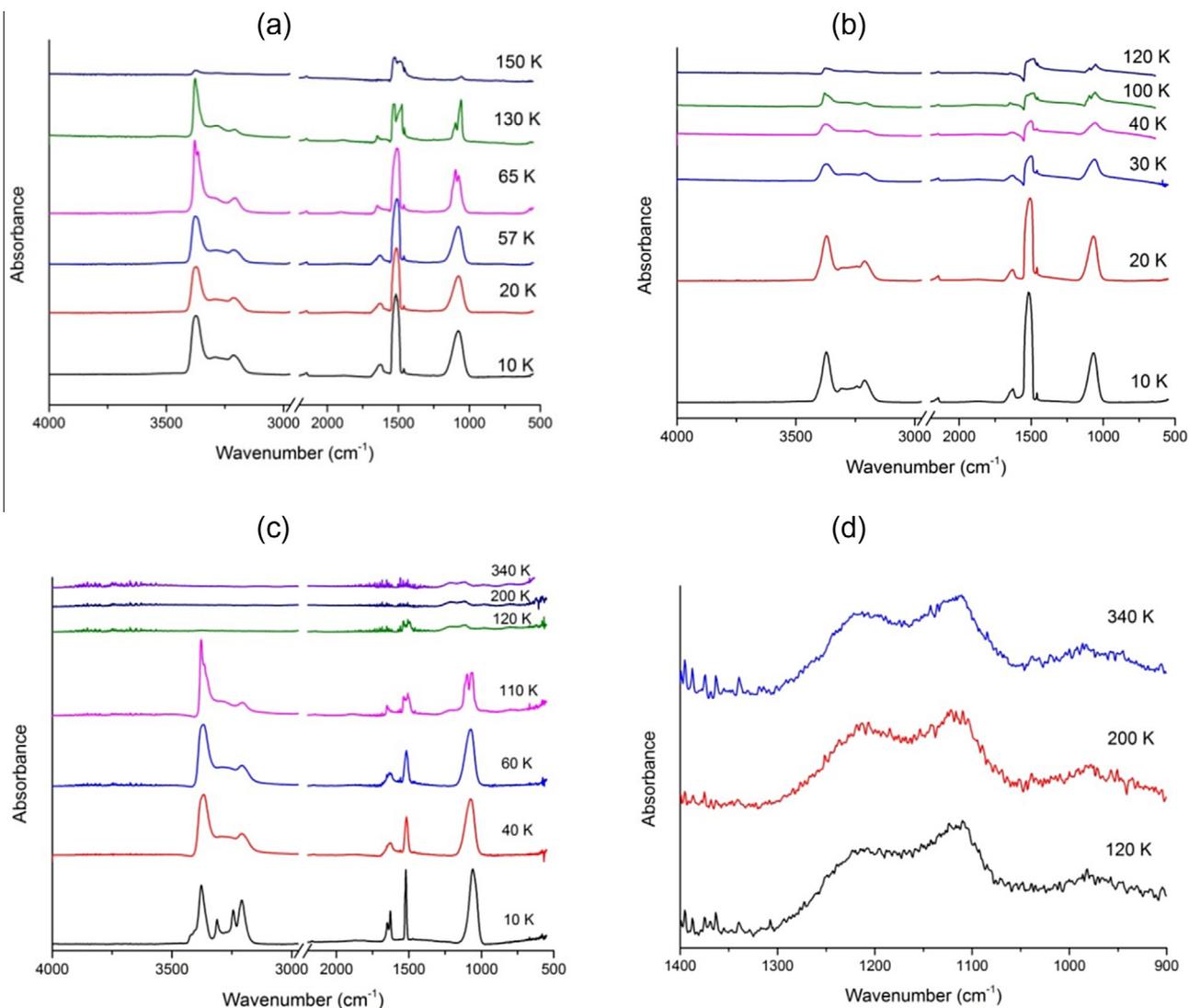


Fig. 3. (a) Temperature dependent infrared spectra of CS_2 below NH_3 deposited at 10 K. (b) Temperature dependent infrared spectra of NH_3 below CS_2 deposited at 10 K. (c) Temperature dependent infrared spectra of mixed deposit of CS_2 and NH_3 deposited at 10 K. (d) Infrared spectra of ammonium dithiocarbamate – residue left behind at higher temperatures upon heating the mixed deposit of CS_2 and NH_3 ices.

Table 2
Column density of ice mixtures as deposited at 10 K.

Ice sample at 10 K	Band (cm ⁻¹)	A value (cm mol ⁻¹)	Column density (No. of molecules)	Ratio CS ₂ :NH ₃
Pure NH ₃ Fig. 1a	1069 cm ⁻¹	*1.63 × 10 ⁻¹⁷	20.29 × 10 ¹⁷	–
Pure CS ₂ Fig. 1b	1520 cm ⁻¹	**9.13 × 10 ⁻¹⁷	18.74 × 10 ¹⁷	–
CS ₂ below NH ₃ Fig. 3a	NH ₃ 1069 cm ⁻¹ CS ₂ 1520 cm ⁻¹	1.63 × 10 ⁻¹⁷ 9.13 × 10 ⁻¹⁷	28.18 × 10 ¹⁷ 7.00 × 10 ¹⁷	1:4
NH ₃ below CS ₂ Fig. 3b	NH ₃ 1069 cm ⁻¹ CS ₂ 1520 cm ⁻¹	1.63 × 10 ⁻¹⁷ 9.13 × 10 ⁻¹⁷	43.74 × 10 ¹⁷ 7.63 × 10 ¹⁷	1:6
NH ₃ + CS ₂ mixture Fig. 3c	NH ₃ 1069 cm ⁻¹ CS ₂ 1520 cm ⁻¹	1.63 × 10 ⁻¹⁷ 9.13 × 10 ⁻¹⁷	9.28 × 10 ¹⁷ 0.30 × 10 ¹⁷	1:30

References.

* A value for NH₃; Bouilloud et al. (2015).

** A value for CS₂; Garozzo et al. (2010).

ature found in the layered deposits, 85 K for CS₂ and 70 K for NH₃ (Table 1). This could be due to NH₃ and CS₂ present as mixed ices where the molecules have to segregate from the mixture to crystallize.

From the temperature dependent spectra in Fig. 3(c) we infer that even after the sublimation of the NH₃ and CS₂ ices above 110 K, there was a residue left behind which was present (1000–1300 cm⁻¹) even after the sample was warmed to 340 K (Fig. 3(d)). There are two broad absorption bands, one centered at 1220 cm⁻¹ and the other centered at 1110 cm⁻¹. Based on the band positions (Knoeck and Witt, 1976) this could be ammonium dithiocarbamate that have been synthesized, via reaction given in Eq. (1) (Mathes et al., 2007), by warming the icy mixture of NH₃ and CS₂ formed at 10 K. In an earlier experiment ammonium carbamate synthesis from a mixture of NH₃ and CO₂ was reported (Bossa et al., 2008a,b; Jheeta et al., 2012; Lv et al., 2014; Noble et al., 2014; Rodriguez-Lazcano et al., 2014). Therefore, due to the sulfur bearing parent molecule it is likely that the sulfur residue observed in our experiment is a thio compound.



The thermal reaction of NH₃ and CS₂ is likely to be very similar to the reaction of NH₃ and CO₂. Bossa et al. (2008b) studied reaction of 1:1 mixtures of NH₃ and CO₂ and found that 49% of CO₂ sublimates out without reacting with NH₃ and the rest likely react with NH₃ thermally and form two products ammonium carbamate and carbamic acid in 1:1 ratio. Noble et al. (2014) extended this to study the kinetics of this reaction, and came out with the conclusion that the reaction is mostly first order with respect to CO₂ in the temperature range of 70–90 K. The reaction is not possible in CO₂ dominated ice, while NH₃ dominated ice gives only ammonium carbamate and not carbamic acid.

Extending this to our experiment of NH₃ with CS₂, considering a similar case, we have calculated the column density in all our samples. It is summarized in Table 2. Here the mixture ice (CS₂ + NH₃) was in 1:30 ratio and

hence we propose the residue which we observed are likely to be ammonium dithiocarbamate and there may be a possibility of formation of dithiocarbamic acid if CS₂ and NH₃ are in 1:1 ratio, which need to be further studied.

4. Conclusion and implication

NH₃ and CS₂ mixtures were studied in astrochemical conditions. The two new bands observed in NH₃ ices revealed the formation of NH₃ homo-dimers which was found to reorient upon heating to 40 K indicating a phase of highly porous NH₃ ice at 10 K. Phase change temperature of NH₃ and CS₂ was found to be 5 K higher in order to segregate whilst present as mixtures in comparison to the phase change temperature of the layered deposits; 65 K and 80 K, respectively. The ice mixture upon warming to higher temperature leaves a residue on the substrate that is even seen in the spectrum recorded at 340 K. Based on the thermal reaction pathway involving NH₃ and CS₂ mixture the residue obtained is believed to be thio compound; ammonium dithiocarbamate.

We propose that efforts must be taken to detect the presence of the complex thio residue such as ammonium dithiocarbamate on comets carrying CS₂ and NH₃. The formation of the thio residue is quite likely due to thermal processing of ices as the temperature increases while the comet gets close to the Sun. Also the stability of such complex molecules even at 340 K suggest that repeated processing of a periodic comet would have higher concentration of the thio residue. Therefore, the periodic comets (known to contain NH₃ and CS₂) could be the good candidates to look for such complex thio molecules.

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References

- Altenhoff, W.J., Batrla, W.K., Huchtmeier, W.K., Schmidt, J., Stumpff, P., Walmsley, M., 1983. Radio observations of comet 1983 D. *Astron. Astrophys.* 125.
- Bossa, J.-B., Borget, F., Duvernay, F., Theule, P., Chiavassa, T., 2008a. Formation of neutral methylcarbamic acid (CH_3NHCOOH) and methylammonium methylcarbamate [$\text{CH}_3\text{NH}_3^+[\text{CH}_3\text{NHCO}_2^-]$] at low temperature. *J. Phys. Chem. A* 112, 5113–5120.
- Bossa, J.B., Theule, P., Duvernay, F., Borget, F., Chiavassa, T., 2008b. Carbamic acid and carbamate formation in $\text{NH}_3:\text{CO}_2$ ices – UV irradiation versus thermal processes. *Astron. Astrophys.* 492, 719–724.
- Bouilloud, M., Fray, N., Bénilan, Y., Cottin, H., Gazeau, M.-C., Jolly, A., 2015. Bibliographic review and new measurements of the infrared band strengths of pure molecules at 25 K: H_2O , CO_2 , CO , CH_4 , NH_3 , CH_3OH , HCOOH and H_2CO . *MNRAS* 451, 2145–2160.
- Dows, D.A., Whittle, E., Pimentel, G.C., 1955. Infrared spectrum of solid ammonium azide: A vibrational assignment. *J. Chem. Phys.* 23, 1475–1479.
- Flynn, G.J., Bleuet, P., Borg, J., Bradley, J.P., Brenker, F.E., Brennan, S., Bridges, J., Brownlee, D.E., Bullock, E.S., Burghammer, M., Clark, B. C., Dai, Z.R., Daghlian, C.P., Djouadi, Z., Fakra, S., Ferroir, T., Floss, C., Franchi, I.A., Gainsforth, Z., Gallien, J.-P., Gillet, P., Grant, P.G., Graham, G.A., Green, S.F., Grossemey, F., Heck, P.R., Herzog, G.F., Hoppe, P., Hoerz, F., Huth, J., Ignatyev, K., Ishii, H. A., Janssens, K., Joswiak, D., Kearsley, A.T., Khodja, H., Lanzirrotti, A., Leitner, J., Lemelle, L., Leroux, H., Luening, K., MacPherson, G. J., Marhas, K.K., Marcus, M.A., Matrajt, G., Nakamura, T., Nakamura-Messenger, K., Nakano, T., Newville, M., Papanastassiou, D.A., Pianetta, P., Rao, W., Riekel, C., Rietmeijer, F.J.M., Rost, D., Schwandt, C.S., See, T.H., Sheffield-Parker, J., Simionovici, A., Sitnitsky, I., Snead, C.J., Stadermann, F.J., Stephan, T., Stroud, R. M., Susini, J., Suzuki, Y., Sutton, S.R., Taylor, S., Teslich, N., Troadec, D., Tsou, P., Tsuchiyama, A., Uesugi, K., Vekemans, B., Vicenzi, E.P., Vincze, L., Westphal, A.J., Wozniakiewicz, P., Zinner, E., Zolensky, M.E., 2006. Elemental compositions of comet 81P/Wild 2 samples collected by stardust. *Science* 314, 1731–1735 (Washington, DC, U.S.).
- Fresneau, A., Danger, G., Rimola, A., Theule, P., Duvernay, F., Chiavassa, T., 2014. Trapping in water – an important prerequisite for complex reactivity in astrophysical ices: the case of acetone ($\text{CH}_3)_2\text{C}=\text{O}$ and ammonia NH_3 . *Mon. Not. R. Astron. Soc.* 443, 2991–3000.
- Garozzo, M., Fulvio, D., Kanuchova, Z., Palumbo, M.E., Strazzulla, G., 2010. The fate of S-bearing species after ion irradiation of interstellar icy grain mantles. *A&A* 509, A67.
- Jackson, W.M., Scodinu, A., Xu, D., Cochran, A.L., 2004. Using the ultraviolet and visible spectrum of comet 122P/de vico to identify the parent molecule CS_2 . *Astrophys. J. Lett.* 607, L139.
- Jheeta, S., Ptasinska, S., Sivaraman, B., Mason, N.J., 2012. The irradiation of 1:1 mixture of ammonia: carbon dioxide ice at 30 K using 1 keV electrons. *Chem. Phys. Lett.* 543, 208–212.
- Knoeck, J., Witt, J., 1976. Infrared and Raman spectra and Urey–Bradley force fields for dithiocarbamate and dithiocarbamate- d_2 anions. Use of a correlation matrix to determine force field uniqueness. *Spectrochim. Acta, Part A* 32, 149–155.
- Lv, X.Y., Boduch, P., Ding, J.J., Domaracka, A., Langlinay, T., Palumbo, M.E., Rothard, H., Strazzulla, G., 2014. Thermal and energetic processing of ammonia and carbon dioxide bearing solid mixtures. *Phys. Chem. Chem. Phys.* 16, 3433–3441.
- Maity, S., Kaiser, R.I., 2013. Electron irradiation of carbon disulfide-oxygen ices: toward the formation of sulfur-bearing molecules in interstellar ices. *Astrophys. J.* 773, 184/181–184/188.
- Maity, S., Kim, Y.S., Kaiser, R.I., Lin, H.M., Sun, B.J., Chang, A.H.H., 2013. Thermal and energetic processing of ammonia and carbon dioxide bearing solid mixtures. *Chem. Phys. Lett.* 577, 42–47.
- Mangum, J.G., Darling, J., Henkel, C., Menten, K.M., MacGregor, M., Svoboda, B.E., Schinnerer, E., 2013. On the detection of higher order carbon sulfides (CS_x ; $x=4-6$) in low temperature carbon disulfide ices. *Astrophys.* 1–29, arXiv.org, arXiv:1310.6586v1311 [astro-ph.GA].
- Mathes, R.A., Booth, H.S., Kirk, R.D., 2007. Ammonium dithiocarbamate. *Inorganic syntheses. Ammonium Dithiocarbamate*. John Wiley & Sons Inc, pp. 48–50.
- McKeegan, K.D., Aleon, J., Bradley, J., Brownlee, D., Busemann, H., Butterworth, A., Chaussidon, M., Fallon, S., Floss, C., Gilmour, J., Gounelle, M., Graham, G., Guan, Y., Heck, P.R., Hoppe, P., Hutcheon, I.D., Huth, J., Ishii, H., Ito, M., Jacobsen, S.B., Kearsley, A., Leshin, L.A., Liu, M.-C., Lyon, I., Marhas, K., Marty, B., Matrajt, G., Meibom, A., Messenger, S., Mostefaoui, S., Mukhopadhyay, S., Nakamura-Messenger, K., Nittler, L., Palma, R., Pepin, R.O., Papanastassiou, D.A., Robert, F., Schlutter, D., Snead, C.J., Stadermann, F.J., Stroud, R., Tsou, P., Westphal, A., Young, E.D., Ziegler, K., Zimmermann, L., Zinner, E., 2006. Isotopic compositions of cometary matter returned by stardust. *Science* 314, 1724–1728 (Washington, DC, U.S.).
- Niemann, H.B., Atreya, S.K., Bauer, S.J., Carignan, G.R., Demick, J.E., Frost, R.L., Gautier, D., Haberman, J.A., Harpold, D.N., Hunten, D. M., Israel, G., Lunine, J.I., Kasprzak, W.T., Owen, T.C., Paulkovich, M., Raulin, F., Raaen, E., Way, S.H., 2005. The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe. *Nature* 438, 779–784.
- Noble, J.A., Theule, P., Duvernay, F., Danger, G., Chiavassa, T., Ghesquiere, P., Mineva, T., Talbi, D., 2014. Kinetics of the NH_3 and CO_2 solid-state reaction at low temperature. *Phys. Chem. Chem. Phys.* 16, 23604–23615.
- Rodriguez-Lazcano, Y., Mate, B., Herrero, V.J., Escribano, R., Galvez, O., 2014. The formation of carbamate ions in interstellar ice analogues. *Phys. Chem. Chem. Phys.* 16, 3371–3380.
- Sivaraman, B., 2016. Electron irradiation of carbon dioxide-carbon disulphide ice analog and its implication on the identification of carbon disulphide on moon. *J. Chem. Sci.* 128 (1), 159–164.
- Sivaraman, B., Raja Sekhar, B.N., Jones, N.C., Hoffmann, S.V., Mason, N.J., 2012. VUV spectroscopy of formamide ices. *Chem. Phys. Lett.* 554, 57–59.
- Sivaraman, B., Raja Sekhar, B.N., Nair, B.G., Hatode, V., Mason, N.J., 2013. Infrared spectrum of formamide in the solid phase. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 105, 238–244.
- Smith, A.M., Stecher, T.P., Casswell, L., 1980. Production of carbon, sulfur, and CS in Comet West. *Astrophys. J.* 242, 402–410.
- Wright, I.P., Sheridan, S., Barber, S.J., Morgan, G.H., Andrews, D.J., Morse, A.D., 2015. CHO-bearing organic compounds at the surface of 67P/Churyumov-Gerasimenko revealed by Ptolemy. *Science* 349, aab0673.
- Yamada, H., Person, W.B., 1964. Absolute infrared intensities of the fundamental absorption bands in solid CS_2 . *J. Chem. Phys.* 40, 309–321.
- Zheng, W., Kaiser, R.I., 2007. An infrared spectroscopy study of the phase transition in solid ammonia. *Chem. Phys. Lett.* 440, 229–234.