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Ethane ices in the outer Solar System: Spectroscopy and chemistry

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ABSTRACT

We report recent experiments on ethane ices made at temperatures applicable to the outer Solar System. New near- and mid-infrared data for crystalline and amorphous ethane, including new spectra for a seldom-studied solid phase that exists at 35–55 K, are presented along with radiation-chemical experiments showing the formation of more-complex hydrocarbons.

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Ethane (C_2H_6) is both an ice on Solar-System bodies and is one of the more-commonly found gas-phase hydrocarbons. Papers reporting C_2H_6 detections are in the literature for Pluto and other TNOs, clouds of Titan, and cometary comae (e.g., Brown et al., 2007; Sasaki et al., 2005; Griffith et al., 2006; Mumma et al., 1996). However, the planetary science literature contains few laboratory-based papers on C_2H_6 ices at temperatures applicable to the outer Solar System. This contrasts sharply with the literature available for methane-containing ices, to which we and others have contributed (e.g., Hudson and Moore, 2001).

Here, we present new experiments on ethane ices including infrared (IR) spectra of amorphous and crystalline phases, information on thermally-induced changes, and radiation-chemical products. These results are relevant to continuing studies of the outer Solar System, such as ground-based observational campaigns, the New Horizons mission, and supporting laboratory work. As an example of the latter, an earlier study of amorphous C_2H_6-containing ices at 10 K (Boudin et al., 1998) reported about a dozen IR band intensities all scaled to a paper with only a single measurement, at only two wavelengths, at a temperature much higher than 10 K, and for a different ice phase (Dows, 1966). An observational example of the need for ethane data is provided by the paper of Brown et al. (2007) on hydrocarbons on KBO 2005 FY_9, in which reference spectra of only crystalline ethane and dissolved ethane were readily available.

Frozen ethane exists in at least four crystalline phases and one amorphous one. At the low pressures of interest here, two of the crystalline phases exist only in the 89.68–90.32 K interval (Schutte et al., 1987), and will not be discussed in this paper. A third crystalline form is stable under 89 K, and has been designated variously as the α phase (Konstantinov et al., 2006), phase II (Pearl et al., 1991; Quirico and Schmitt, 1997), and phase III (Schutte et al., 1987). We will refer to it as simply crystalline ethane. A fourth crystalline form has been reported and termed "metastable ethane" by Wisnosky et al. (1983), a designation we also will employ, without any implications as to phase stability.

Fig. 1 shows IR transmission spectra of ethane ices made by vapor-phase deposition of room-temperature C_2H_6 onto a KBr substrate, pre-cooled to the temperatures indicated. Ethane ice formation below about 30 K always resulted in amorphous C_2H_6 (Fig. 1a). Samples made at 30–55 K were composed mainly, if not entirely, of metastable C_2H_6 (Fig. 1b), and depositions above about 60 K always gave crystalline ethane (Fig. 1c), with phase assignments being made with reference to literature spectra. At ∼70 K and higher, ethane rapidly sublimed in our vacuum system. Warming either amorphous ethane to 40 K or metastable ethane to 65 K irreversibly converted the sample to the crystalline phase, and the resulting spectrum is shown at the top of Fig. 1. We emphasize that the metastable phase could only be made by direct deposition in the 30–55 K region and never by warming an amorphous ice or cooling a crystalline one. The near-IR region in Fig. 1 has been expanded to better show the differences in band shapes and relative intensities for the three phases. Table 1 summarizes solid-phase ethane positions and relative band areas.

Of the three phases treated here, crystalline ethane is the only one for which mid-IR optical constants are available (Pearl et al., 1991). The latter allowed us to scale all spectra in Fig. 1 to the same ethane column density by first warming amorphous and metastable samples to crystallize them, without mass loss. Each original sample's ethane abundance (N) was then calculated from the absorbance of any peak in the resulting crystalline sample's spectrum by

$$N = 2.303 \times \text{absorbance} \times \text{density} \times 6.022 \times 10^{23} / (\alpha \times \text{molecular mass})$$

where α is the peak's absorption coefficient (Pearl et al., 1991). This procedure gave $N = 9.6 \times 10^{17}$ molecules/cm^2 for Fig. 1c, and the other spectra shown have been scaled to match this value. We also note that only crystalline ethane's mass density is known, 0.719 g/cm^3 from Van Nes and Vos (1978), preventing a direct determination of either column density or IR intrinsic band strengths for the other two phases.

Icy bodies in both the Solar System and the interstellar medium experience chemical alterations by a combination of cosmic rays, magnetospheric radiation, and vacuum-UV photons. While each of these induces changes by distinct reaction mechanisms, the final photo- and radiation-chemical products in each case are similar if not identical (Hudson et al., 2001). To study such alterations, we exposed frozen C_2H_6 to a beam of 0.8 MeV protons from a Van de Graaff accelerator. The spectra before and after irradiation at ∼20 K are shown in Fig. 2 with major products identified. In general, neither calculated nor gas- or liquid-phase spectra are sufficient for assigning solid-phase IR bands in ice mixtures, and so each identification in Fig. 2 was made by comparison to a solid-phase spectrum for the compound indicated. Products identified include CH_4, C_2H_2, C_2H_4, C_3H_4, C_3H_6, C_3H_8, and C_4H_{10}. This appears to be the first *in situ* identification of many of these radiation products at an

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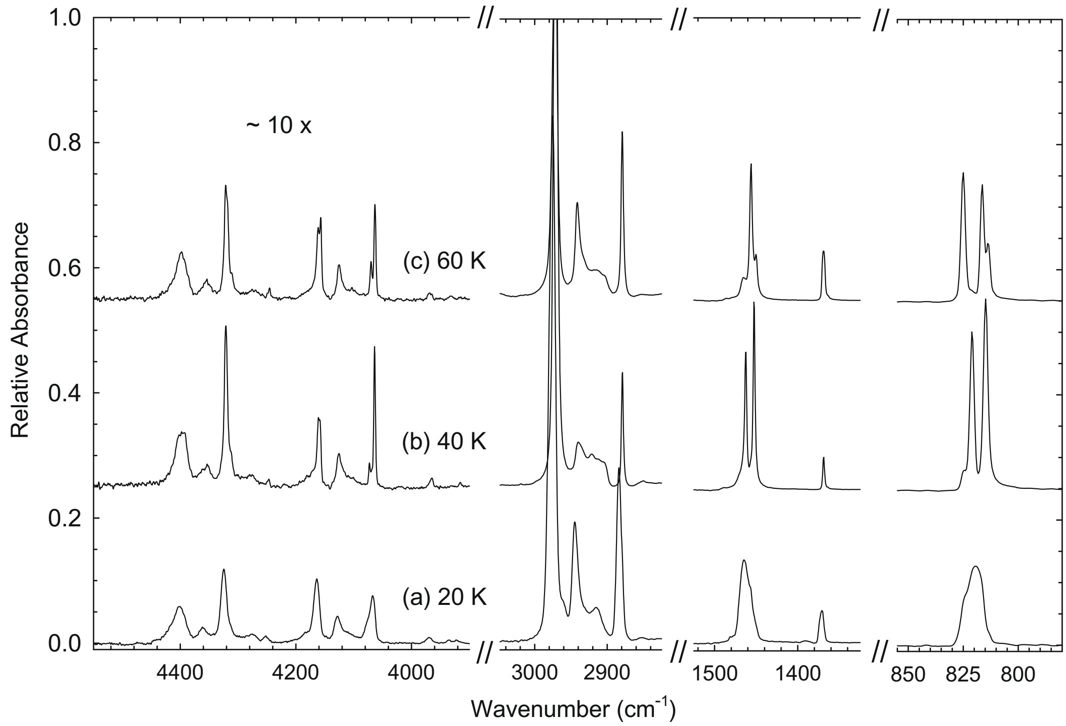

Fig. 1. IR spectra at 2-cm^{-1} resolution for (a) amorphous, (b) metastable, and (c) crystalline ethane, offset and scaled for a common molecular column density of about 9.6×10^{17} molecules/cm^2. Note the 10-fold vertical expansion in the left-hand panel, the non-uniformity of the horizontal scale, and that the intense feature near 2970 cm^{-1} extends off the vertical scale.

Table 1
Selected IR spectral regions of solid forms of ethane, along with relative areas and wavenumber positions (cm^{-1}) and wavelengths (μm), in parentheses, for major peaks within each spectral region.

Spectral region	Amorphous 20 K		Metastable 40 K		Crystalline 60 K	
	Relative area	Peak position	Relative area	Peak position	Relative area	Peak position
4442–4374	0.011	4401 (2.272)	0.024	4398 (2.274)	0.024	4398 (2.274)
4337–4295	0.011	4325 (2.312)	0.028	4321 (2.314)	0.024	4320 (2.315)
4200–4141	0.011	4164 (2.402)	0.022	4160 (2.404)	0.023	4157 (2.406)
4085–4047	0.008	4067 (2.459)	0.012	4064 (2.461)	0.013	4063 (2.461)
3020–2890	1.00	2976 (3.360)	1.00	2971 (3.366)	1.00	2972 (3.365)
2895–2866	0.18	2884 (3.467)	0.058	2879 (3.473)	0.14	2879 (3.437)
1500–1420	0.17	1464 (6.817)	0.20	1463 (6.835) 1453 (6.882)	0.21	1464 (6.817) 1456 (6.868) 1451 (6.892)
1380–1355	0.026	1371 (7.294)	0.014	1369 (7.305)	0.043	1369 (7.305)
835–800	0.094	819 (12.21)	0.14	821 (12.18) 815 (12.27)	0.15	825 (12.12) 816 (12.25)

outer Solar System temperature (i.e., ∼20 K). We note that the identifications in Fig. 2 are based on reference spectra of the molecules indicated, each in a pure, amorphous state. Since each molecule was a hydrocarbon of low or zero polarity, it was not necessary to obtain reference spectra of each molecule trapped in ethane, also an apolar hydrocarbon. We further note that the radiation dose we used, ∼22 eV/C_2H_6 molecule, is about that expected for the uppermost 1 μm of a TNO over ∼0.5 Gyr at ∼50 AU. Current estimates of TNO dose are given by Hudson et al. (2008) and references therein.

The experiment represented by Fig. 2 also was used to determine that a dose of ∼22 eV/molecule was sufficient to destroy about 33% of the original C_2H_6 molecules at ∼20 K. Irradiations at 9 and 30 K gave results qualitatively similar to those shown in Fig. 2. In other words, the radiation dose, not the ice temperature or phase, determined

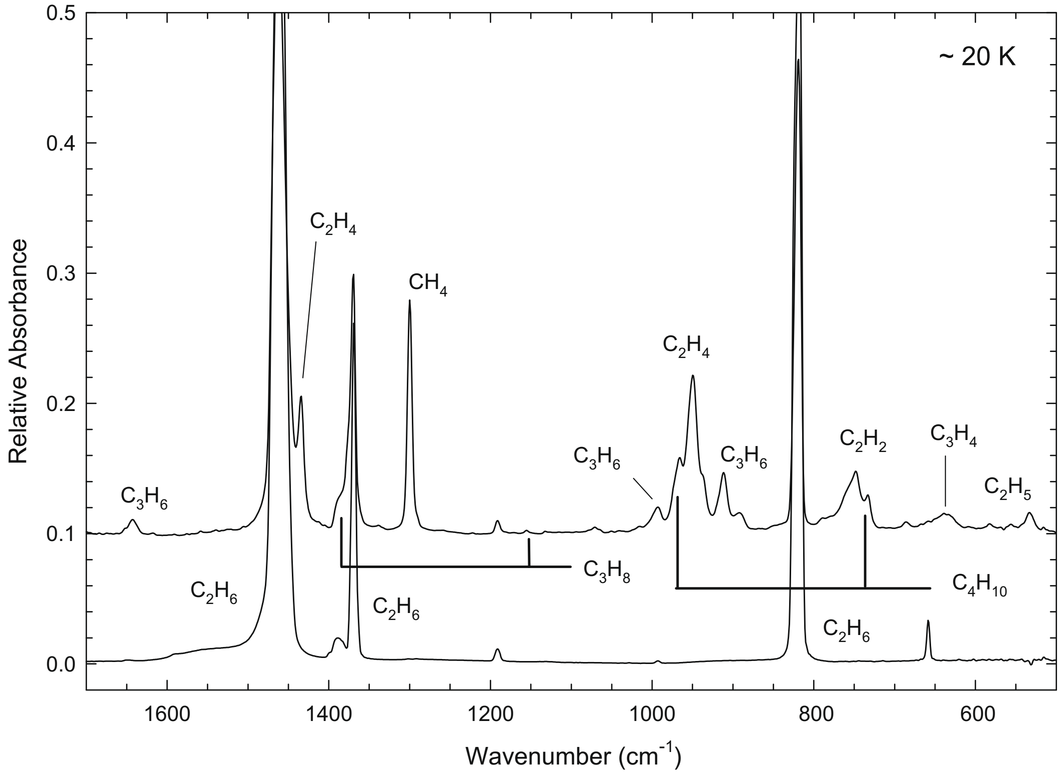

Fig. 2. IR spectra of amorphous C_2H_6 before (lower) and after irradiation to a dose of about 22 eV per ethane molecule at ∼20 K with 0.8 MeV H^+. A confirmatory band for C_3H_8 was found at 2959 cm^{-1} (not shown). A small feature in the lower right-hand corner near at 660 cm^{-1} is due to background CO_2.

the reaction products; further work is needed for a quantitative comparison. Warming the irradiated sample of Fig. 2 to ∼150 K and higher gave a residual hydrocarbon material with an IR spectrum essentially identical to that found for energetically-processed CH_4 (Dartois et al., 2004, Fig. 1) and which contains spectral features seen in the diffuse interstellar medium (Pendleton and Allamandola, 2002, Fig. 8).

Butane formation in our experiments is particularly interesting since it suggests that the lengthening of ethane's carbon chain occurred by the coupling of ethyl radicals (C_2H_5) made from ethane itself. The C_2H_5 infrared feature at 532 cm^{-1} in the upper trace of Fig. 2 supports this interpretation. No IR band for the methyl radical (CH_3, 619 cm^{-1}) was seen in the present experiments, unlike in our earlier work on irradiated CH_4 ices (Moore and Hudson, 2003). Observation of the sequence

$$2C_2H_6 \rightarrow 2C_2H_5 \rightarrow C_4H_{10}$$

is important for understanding the extension of carbon chains needed to make both biomolecules and refractory organic residues. It is possible that the three-carbon products indicated in Fig. 2 resulted from butane decomposition, but further work is needed to test this suggestion. Calculating an ethane-to-butane conversion was made difficult by the overlap of spectral bands, but it was estimated that about 40 ± 10% of the ethane lost was converted to C_4H_{10}. Our unpublished band strengths for butane were used for this estimate: $A(1464\ cm^{-1}) = 2.9 \times 10^{18}$ cm/molecule and $A(1464\ cm^{-1}) = 1.4 \times 10^{18}$ cm/molecule (Peeters et al., in preparation).

Our results generally agree with what little has been published on ethane ices. The band shapes and positions in Fig. 1 agree with earlier work, but the lack of either a common vertical scale or full spectra by either Tejada and Eggers (1976) or Wisnosky et al. (1983) make intensity comparisons impossible. Our amorphous-C_2H_6 spectrum resembles that of Boudin et al. (1998), although we now report direct measurements of relative band strengths for both near- and mid-IR features. Our spectra of crystalline ethane are almost temperature invariant (14–65 K), and match the 30 K data of Pearl et al. (1991). Quirico and Schmitt (1997) published a near-IR spectrum of ethane condensed at 21 K, but without a phase assignment. Since the relative peak heights of their spectrum do not match those of our amorphous ethane (Fig. 1a), their sample may have had contributions from both the amorphous and metastable phases. As for our radiation results, Strazzulla et al. (2002) observed that irradiation of C_2H_6 at 12 K by 30 keV He^+ ions produces CH_4, C_2H_4, and C_2H_2, the latter two by hydrogen elimination. We have found similar results here (Fig. 2) and earlier for other compounds (Moore and Hudson, 2003).

The present work argues for additional study of each ethane phase considered here. Pure C_2H_6 ice forming in environments below ∼30 K will be amorphous (Fig. 1a) and more efficient at trapping other molecules than will crystalline C_2H_6. Exposure of CH_4-containing ices to radiation will produce amorphous C_2H_6 a major product (Moore and Hudson, 2003). Pure C_2H_6 forming at 30–60 K, such as on Pluto (Tryka et al., 1994), is expected to be in the metastable phase (Fig. 1b). Above 60 K, crystalline-phase ethane (Fig. 1c) will dominate. Finally, it will be difficult to detect pure surficial C_2H_6 ice above ∼70 K without some type of overpressure. All of this suggests that detailed IR studies of ethane frozen on TNOs and elsewhere require data for the correct molecular phase at relevant temperatures, with and without radiation processing. We are now measuring the needed spectra and optical constants, and extending the radiation experiment of Fig. 2 into the near-IR region.

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References

Boudin, N., Schutte, W.A., Greenberg, J.M., 1998. Constraints on the abundances of various molecules in interstellar ice. Laboratory studies and astrophysical implications. Astron. Astrophys. 331, 749–759.

Brown, M.E., Barkume, K.M., Blake, G.A., Schaller, E.L., Rabinowitz, D.L., Roe, H.G., Trujillo, C.A., 2007. Methane and ethane on the bright Kuiper belt object 2005 FY9. Astron. J. 133, 284–289.

Dartois, E., Munoz-Caro, G.M., Deboffle, D., d'Hendecourt, L., 2004. Diffuse interstellar medium organic polymers. Astrophys. J. 423, L33–L36.

Dows, D.A., 1966. Absolute infrared intensities in crystalline acetylene and ethane. Spectrochim. Acta 22, 1479–1481.

Griffith, C.A., and 14 colleagues, 2006. Evidence for a polar ethane cloud on Titan. Science 313, 1620–1622.

Hudson, R.L., Moore, M.H., 2001. Radiation chemical alterations in Solar System ices: An overview. J. Geophys. Res. Planets 106, 33275–33284.

Hudson, R.L., Moore, M.H., Gerakines, P.A., 2001. The formation of cyanate ion (OCN^-) in interstellar ice analogues. Astrophys. J. 550, 1140–1150.

Hudson, R.L., Palumbo, M.E., Strazzulla, G., Moore, M.H., Cooper, J.F., Sturner, S.J., 2008. Laboratory studies of the chemistry of transneptunian object surface materials. In: Barucci, M.A., Boehnhardt, H., Cruikshank, D.P., Morbidelli, A. (Eds.), The Solar System beyond Neptune. University of Arizona Press, Tucson, pp. 507–523.

Konstantinov, V.A., Revyakin, V.P., Sagan, V.V., 2006. Rotation of the methyl groups and thermal conductivity of molecular crystals: Ethane. Low Temp. Phys. 32, 689–694.

Moore, M.H., Hudson, R.L., 2003. Infrared study of ion-irradiated N_2-dominated ices relevant to Triton and Pluto: Formation of HCN and HNC. Icarus 161, 486–500.

Mumma, M.J., DiSanti, M.A., Dello Russo, N., Fomenkova, M., Magee-Sauer, K., Kaminski, C.D., Xie, D.X., 1996. Detection of abundant ethane and methane, along with carbon monoxide and water, in Comet C/1996 B2 Hyakutake: Evidence for interstellar origin. Science 272, 1310–1314.

Pearl, J., Ngoh, M., Ospina, M., Khanna, R., 1991. Optical constants of solid methane and ethane from 10,000 to 450 cm^{-1}. J. Geophys. Res. 96, 17477–17482.

Pendleton, Y.J., Allamandola, L.J., 2002. The organic refractory material in the diffuse interstellar medium: Mid-infrared spectroscopic constraints. Astrophys. J. 138, 75–98.

Quirico, E., Schmitt, B., 1997. Near-infrared spectroscopy of simple hydrocarbons and carbon oxides diluted in solid N_2 and as pure ices: Implications for Triton and Pluto. Icarus 127, 354–378.

Sasaki, T., Kanno, A., Ishiguro, M., Kinoshita, D., Nakamura, R., 2005. Search for nonmethane hydrocarbons on Pluto. Astrophys. J. 618, L57–L60.

Schutte, M.H.M., Prins, K.O., Trappeniers, N.J., 1987. Nuclear magnetic resonance in solid ethane at high pressure. II. The phase diagram of solid ethane. Physica 144B, 357–367.

Strazzulla, G., Baratta, G.A., Domingo, M., Satorre, M.A., 2002. Ion irradiation of frozen C_2H_n (n = 2, 4, 6). Nucl. Instr. Meth. B 191, 714–717.

Tejada, S.B., Eggers Jr., D.F., 1976. Infrared spectra of crystalline ethane and ethane-d_6. Spectrochim. Acta 32A, 1557–1562.

Tryka, K.A., Brown, R.H., Chruikshank, D.P., Owen, T.C., Geballe, T.R., Debergh, C., 1994. Temperature of nitrogen ice on Pluto and its implications for flux measurements. Icarus 112, 513–527.

Van Nes, G.J.H., Vos, A., 1978. Single-crystal structures and electron density distributions of ethane, ethylene, and acetylene. 1. Single-crystal X-ray structure determinations of two modifications of ethane. Acta Cryst. B34, 1947–1956.

Wisnosky, M.G., Eggers, D.F., Fredrickson, L.R., Decius, J.C., 1983. A metastable solid phase of ethane. J. Chem. Phys. 79, 3513–3516.