

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.

Key Words: Ices, IR Spectroscopy; Trans-Neptunian Objects; Cosmic Rays; Organic Chemistry

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

Figure 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 Figure 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.

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 CH₄, C₂H₂, C₂H₄, C₃H₄, C₃H₆, C₃H₈, and C₄H₁₀. This appears to be the first *in situ* identification of many of these radiation products at an 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 / C₂H₆ molecule, is about that expected for the uppermost 1 μ m 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 C₂H₆ 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 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 CH₄ (Dartois et al., 2004, Fig.

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

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Figure Captions

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 ten-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.

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 $\sim 20\text{ K}$ 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 .

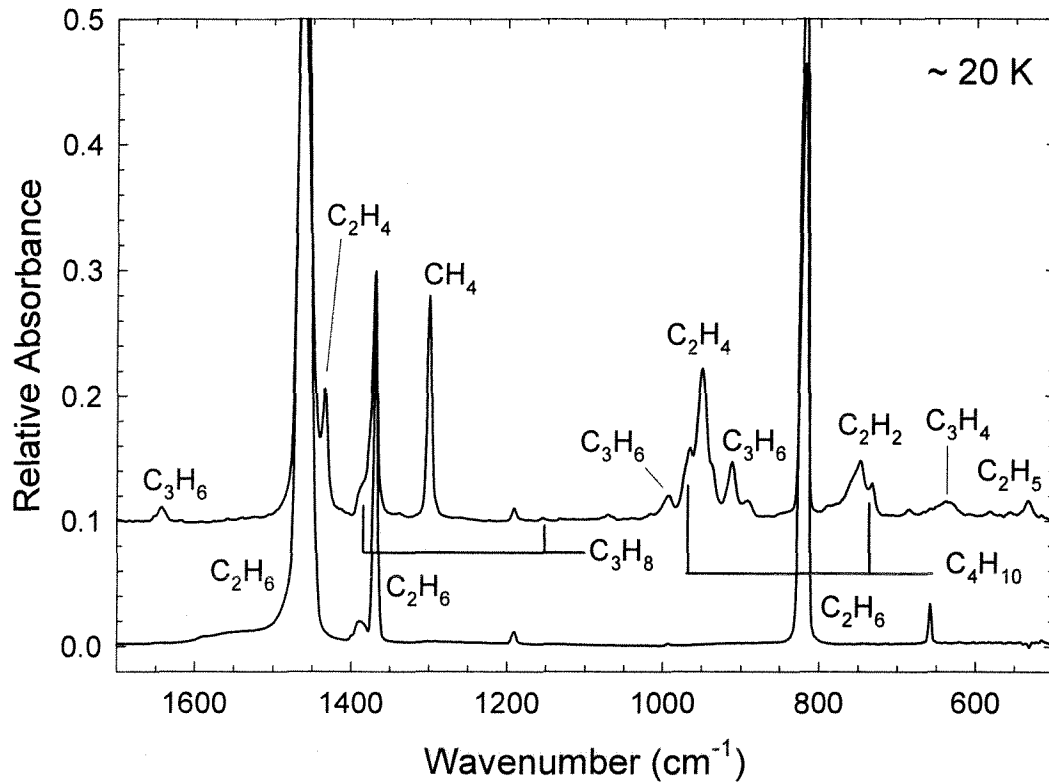


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