Note

# Ethane ices in the outer Solar System: Spectroscopy and chemistry

R.L. Hudson [a,b,*], M.H. Moore [b], L.L. Raines [a]

[a] Department of Chemistry, Eckerd College, St. Petersburg, FL 33711, United States
[b] Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20771, United States

A B S T R A C T

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.

Published by Elsevier Inc.

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 reference 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 $\alpha$ 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
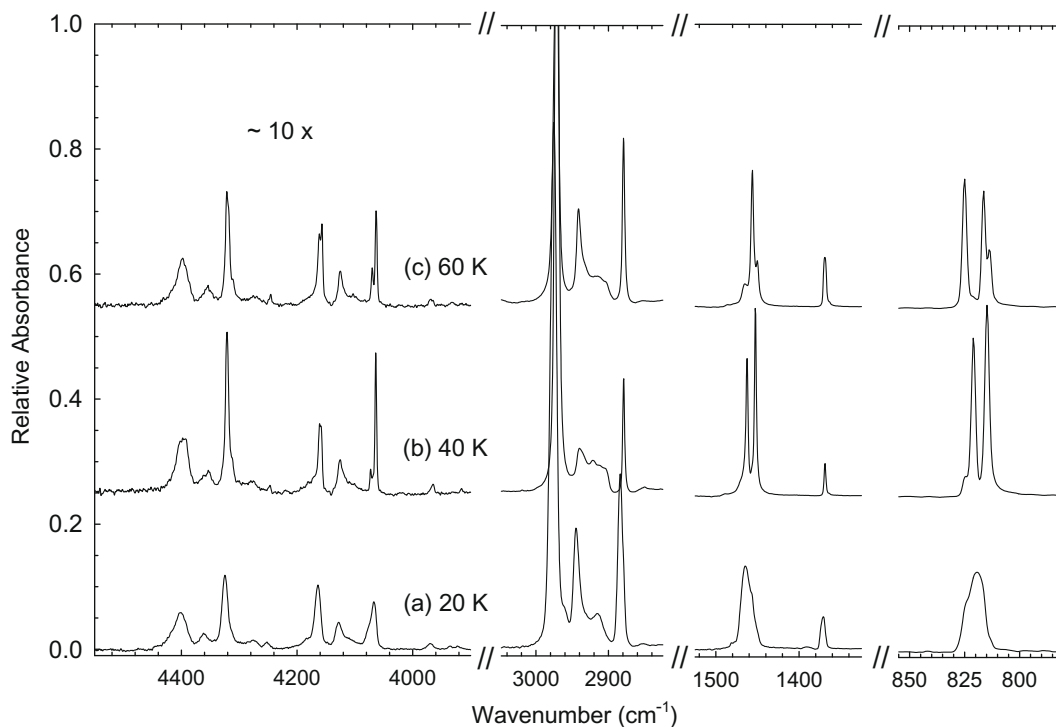
**Fig. 1.** IR spectra at 2-cm$^{-1}$ resolution for (a) amorphous, (b) metastable, and (c) crystalline ethane, offset and scaled for a common molecular column density of about 9.6 × 10$^{17}$ molecules/cm$^2$. Note the 10-fold vertical expansion in the left-hand panel, the non-uniformity of the horizontal 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$_2$H$_6$ 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$_2$H$_6$ 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