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An IR investigation of solid amorphous ethanol — Spectra, properties, and phase changes

Reggie L. Hudson

Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

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ABSTRACT

Mid- and far-infrared spectra of condensed ethanol (CH_3CH_2OH) at 10–160 K are presented, with a special focus on amorphous ethanol, the form of greatest astrochemical interest, and with special attention given to changes at 155–160 K. Infrared spectra of amorphous and crystalline forms are shown. The refractive index at 670 nm of amorphous ethanol at 16 K is reported, along with three IR band strengths and a density. A comparison is made to recent work on the isoelectronic compound ethanethiol (CH_3CH_2SH), and several astrochemical applications are suggested for future study.

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1. Introduction

Some years ago our research group was engaged in the measurement of far-infrared spectra for upcoming NASA and ESA space missions involving infrared instrumentation. Most of our far-IR work was published at the time [1], and has since been used by astronomers and terahertz spectroscopists [2], but a new paper in this journal recently reminded us of some of our unpublished results. The focus of most of our research is infrared spectra of small-molecule amorphous and crystalline solids at 8–250 K, with an emphasis on amorphous ices below 100 K. Their IR spectra are used to study the low-temperature chemistry of interstellar clouds and of extraterrestrial objects in our solar system, such as ice-covered moons and trans-Neptunian objects. See Boogert et al. or Gudipati and Castillo-Rogez for examples [3,4]. To date, astronomical observations from ground- and space-based observatories have provided IR evidence for about a dozen extraterrestrial molecules and ions in the solid phase. Although our title molecule is not among that dozen, laboratory studies of the physical properties and chemical reactions of many yet-undetected species are invaluable for understanding how molecules in extraterrestrial environments can form and evolve.

Of the organic molecules identified in ices by astronomers, methanol (CH_3OH) has received the most detailed and widespread attention, whereas solid ethanol (C_2H_5OH) has almost been ignored by laboratory astrochemists. The recent work of Oba et al. [5] is an exception, making extensive use of earlier IR studies [6,7]. In general, however, a lack of information on amorphous C_2H_5OH, the form expected in many extraterrestrial environments, hinders an understanding, evaluation, and possible observation of ethanol-ice by infrared astronomers. We address this situation in the present paper, beginning with a brief presentation of our earlier far-IR results on amorphous and crystalline ethanol, followed by much newer mid-IR studies. Spectra are presented, apparently for the first time, of amorphous and crystalline ethanol made in a single experiment within the same vacuum chamber. We include values of band strengths for three IR features, a refractive index for amorphous ethanol, a density estimate, and details on phase changes. Our goal is not new detailed spectral analyses and band assignments, but rather the information that IR data can provide on amorphous C_2H_5OH.

2. Experimental

Nearly all of our laboratory procedures and equipment have been described in earlier papers, so a detailed presentation will not be given [8]. Our far-IR spectra were recorded with 4-cm^{-1} resolution on a Mattson Polaris FTIR spectrometer in 1992 using a polyethylene substrate [1]. Our mid-IR spectra were measured recently with a new Thermo iS50 FTIR instrument and a KBr substrate, using 100 scans per spectrum and a resolution of 0.5 cm^{-1}. The high-vacuum chambers (base pressure ~ 10^{-8}) and deposition systems were similar for the two sets of measurements, except that the smaller vacuum chamber had a volume of about 100 cm^3, whereas the larger chamber has a volume of ~300 cm^3. Deposition rates typically gave an increase in the ice's thickness of 1–2 μm h^{-1}. In all cases, the IR beam was unpolarized and perpendicular to the plane of the ice sample. Changes in sample

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E-mail address: reggie.hudson@nasa.gov.

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temperature, both warming and cooling, were conducted with the vacuum chamber open to the interfaced, dedicated turbo-molecular pumps. Ethanol (undenatured absolute) and methanol were purchased from Pharmaco and Sigma Aldrich, respectively, and used as received, aside from degassing with freeze-pump-thaw cycles using liquid nitrogen.

3. Results

Fig. 1 shows far-IR spectra of solid ethanol formed by vapor-phase deposition onto a polyethylene substrate held at 13 K. The spectra are somewhat noisy, but the rounded appearance of the peaks in (a) suggests that the initially formed ethanol-ice was amorphous, as is the case with nearly all organic compounds we have studied under similar conditions. As the ethanol sample was warmed, subtle changes were seen in its spectrum, probably reflecting the solid-phase alterations reported by others [9,10]. However, by 115–120 K, considerable sharpening of all spectral bands was observed, indicating the sample's crystallization. These changes are readily seen by comparing traces (a) and (b) in Fig. 1. Few additional changes were met on further warming to 150–155 K, but at 160 K the IR bands of crystalline ethanol returned to their original rounded shapes, shown in trace (c) and suggesting a loss of crystallinity. Recooling to 13 K gave little further change, but rewarming to 120 K again gave the far-IR spectrum shown in (b) and further warming to ~160 K once more gave a spectrum resembling (c). In other words, a temperature sequence along the lines of (a) → (b) → (c) → (a) from Fig. 1 was followed with the IR spectra showing a gain and loss of crystallinity by the sample in each cycle.

These far-IR changes are consistent with recent mid-IR measurements from our laboratory, as presented in Fig. 2. Again, the initially amorphous ethanol sample of spectrum (a) crystallized on warming to give spectrum (b), and again the spectrum reverted to one resembling that of amorphous ethanol on additional warming, and again the temperature sequence (a) → (b) → (c) → (a) could be followed with the same repetition of spectral changes, subject to one condition described below. The temperatures of (b) and (c) in Fig. 2 were chosen to emphasize the small range over which the (b)-to-(c) conversion took place. Differences between (a) and (c) exist in the 3600–3000 cm^{-1} region, but otherwise the similarities between (a) and (c) are quite pronounced, as shown in the expansion of Fig. 3.

Table 1 lists peak positions of some of the more distinct IR features in our spectra of amorphous and crystalline ethanol. These positions agree with expectations from the literature [11–15], but there are disagreements among previous workers on some of the assignments, mainly those between 1500 and 1300 cm^{-1} and below 400 cm^{-1}, and there is considerable mixing among some of the motions. Some of the identifications are straightforward, such as the broad band near 3200 cm^{-1} being from OH vibrations, the features at 3000–2800 cm^{-1} being from symmetric and asymmetric stretches of CH_3 and CH_2 groups, and the peak near 1050 cm^{-1} being from a C—O stretch.

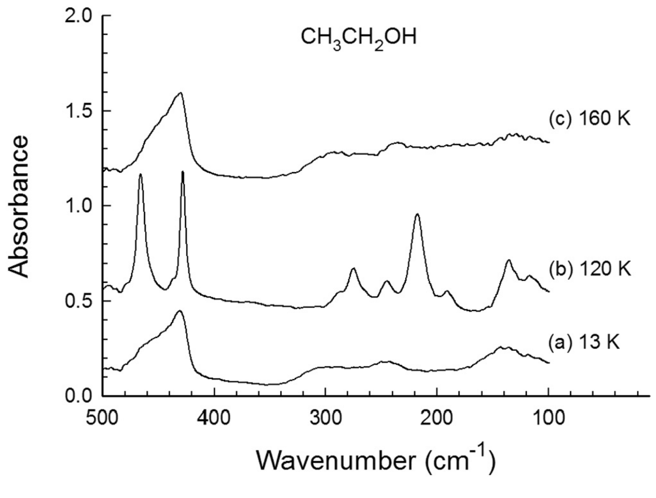

Fig. 1. Far-IR spectra of ethanol deposited at 13 K and warmed to 120 and 160 K. Spectra have been offset vertically for clarity, but not rescaled. The ethanol sample's thickness was not measured accurately at the time, but was ~10 μm.

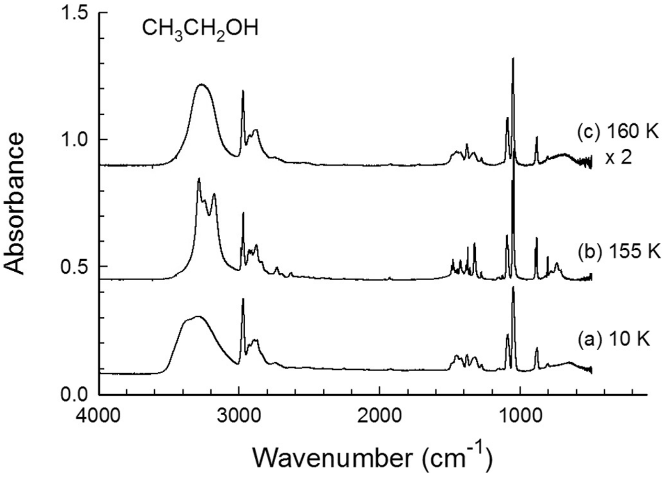

Fig. 2. Mid-IR spectra of ethanol deposited at 10 K and warmed to 155 and 160 K. The sample's original thickness was about 1.5 μm. Spectra have been offset vertically for clarity. Note that the scale of (c) has been expanded by a factor of two to show detail.

Repeated tests with ethanol ices between about 0.5 and 8.0 μm in thickness confirmed that above ~155 K a competition existed between a sample's loss of crystallinity and its loss to our vacuum system. Our thicker ices could be put through the temperature sequence of (a) → (b) → (c) → (a) in Figs. 1–3 multiple times with only small variations in IR intensities, from loss to the vacuum, in each cycle. In contrast, our thinner samples were lost before the (b) → (c) conversion occurred. Burke et al. [11] used temperature-programmed desorption to show that for even thinner ethanol ices the first change, (a) → (b), shows a similar thickness dependence, with no crystallization detected for sufficiently thin samples. In all cases, when our ices were left standing at 160 K they were completely lost in few minutes or less depending on the sample's thickness.

Several observations were made on cooling ethanol samples from 160 K to 10, 80, and 100 K. Recooling the sample of (c) in Fig. 2 to either 10 or 80 K at about 6 K min^{-1} preserved the spectrum's general

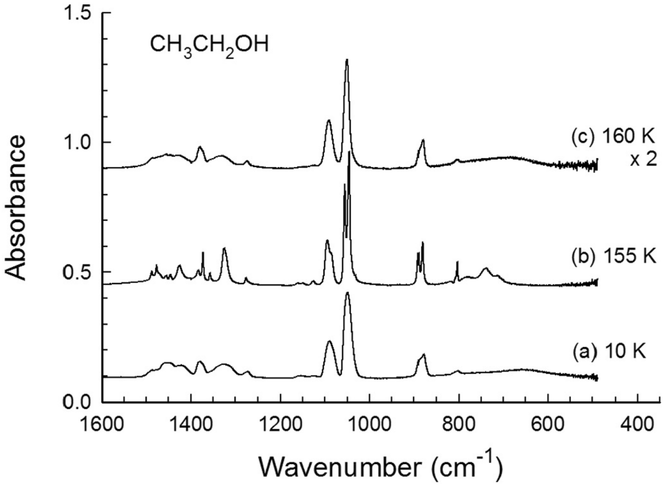

Fig. 3. Expansion of Fig. 2 highlighting the 1600–500 cm^{-1} region. Note the similarity of (a) and (c).

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