IR spectra and properties of solid acetone, an interstellar and cometary molecule

Reggie L. Hudson [a,*], Perry A. Gerakines [a], Robert F. Ferrante [b]

[a] *Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA*
[b] *Chemistry Department, U.S. Naval Academy, Annapolis, MD 21402, USA*

ABSTRACT

Mid-infrared spectra of amorphous and crystalline acetone are presented along with measurements of the refractive index and density for both forms of the compound. Infrared band strengths are reported for the first time for amorphous and crystalline acetone, along with IR optical constants. Vapor pressures and a sublimation enthalpy for crystalline acetone also are reported. Positions of ^{13}C-labeled acetone are measured. Band strengths are compared to gas-phase values and to the results of a density-functional calculation. A 73% error in previous work is identified and corrected.

Published by Elsevier B.V.

1. Introduction

Among the roughly 200 extraterrestrial molecules identified, there are at least two members of nearly every type of common organic compound, such as alkanes, alkenes, alkynes, aromatics, alcohols, amines, nitriles, ethers, epoxides, and mercaptans (thiols). From the carbonyl-containing classes, there are at least two interstellar identifications each of common aldehydes, esters, acids, and amides. The lone exception is the ketones, for which only acetone, the prototypical ketone, has been identified.

Our interest in solid acetone arises from its possible role as a degradation product of propylene oxide, a recently discovered interstellar molecule [1]. However, solid acetone is of interest in itself as it has been detected both in the interstellar medium and on the surface of a comet [2,3]. The reactions for the formation and destruction of acetone are unclear, but although they almost certainly involve solid-phase chemistry the lack of quantitative data on solid acetone hinders studies of this molecule.

An example of the problems to which a lack of acetone data can lead is found in a recent paper on the irradiation of acetone ices at 16 K [4]. Lacking solid-phase IR band strengths, the authors used the results of a density-functional theory (DFT-B3LYP) calculation by others [5] to estimate the thickness of their acetone samples. Here we show that that approach led to a 73% error in acetone abundance, which propagated through the authors' subsequent work on product abundances, reaction

cross sections, and an attempt at a mass-balance calculation. Moreover, the phase or state of the authors' acetone ices was not given and there is little in the literature with which to compare.

In the present paper we present new mid-infrared spectra of amorphous and crystalline acetone along with band strengths and optical constants. We also report measurements of a refractive index and density for both forms of the compound. As an example of one use of this new information, we have measured vapor pressures and a sublimation enthalpy for crystalline acetone. IR positions of ^{13}C-labeled acetone also have been measured, apparently for the first time. Band strength results are compared to gas-phase values and a density-functional calculation. These new results will be useful to laboratory astrochemists and others studying the formation and reactions of acetone in a variety of extraterrestrial environments.

2. Experimental

Most of our procedures and equipment can be found in our recent papers, and so only a summary is given here [6].

All samples were prepared by vapor-phase condensation onto a KBr substrate (area $\approx$ 5 cm^2) precooled within a vacuum system (~10^{-8}–10^{-10} Torr). Depositions were at ~10 K to make amorphous samples and at ~125 K to make crystalline ones, usually at a rate that gave a growth in ice thickness of about 1 μm h^{-1} as measured with interference fringes. Transmission IR spectra were recorded with a Thermo iS50 spectrometer using an unpolarized IR beam aligned perpendicular to the ice's surface. Spectra typically were recorded from 4000 to 400 cm^{-1} using 200 scans at 1-cm^{-1} resolution.
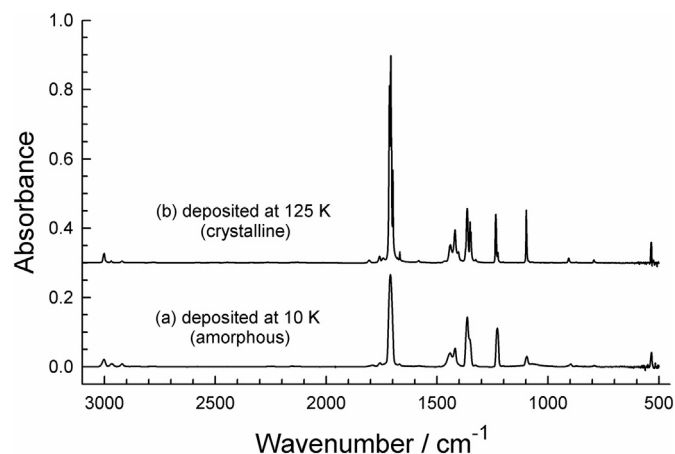
Fig. 1. Survey infrared spectra of acetone deposited at (a) 10 and (b) 125 K. Spectra were recorded at the temperature of deposition and have been offset for clarity. Initial thicknesses were about 0.5 and 0.6 μm for the 10 and 125 K ices, respectively.

Solid acetone's density (ρ) and refractive index (n) were measured inside a stainless-steel ultra-high vacuum (UHV) chamber (~10^{-10} Torr). Ices were grown on the gold-coated surface of an INFICON quartz-crystal microbalance (QCM) for density measurements [6]. During the growth of each ice, two 670-nm lasers generated interference fringes from the surface of the substrate. Measuring the period of each laser's fringes allowed the calculation of n in the usual way. Again, see our earlier papers or, from another laboratory, the work of Satorre et al. [7] As a check on our work, we also measured n_{670} with the two-laser interferometer we have used in the past [8]. Results from the two systems agreed within experimental error. Both systems also were interfaced to IR spectrometers so that the phase and quality of each ice sample could be checked.

Acetone and acetone-2-^{13}C (carbonyl position labeled) were purchased from Sigma-Aldrich and degassed with liquid nitrogen and freeze-pump-thaw cycles before use.

3. Results

3.1. Refractive Indices and Densities

Refractive indices at 670 nm (n_{670}) were measured in triplicate and gave $n_{670} = 1.335$ for amorphous acetone at 20 K and $n_{670} = 1.453$ for crystalline acetone at 125 K, with a standard error of about ± 0.002 in each case. Measurements of density (ρ) resulted in values of 0.783 and 0.999 g cm^{-3} for amorphous and crystalline acetone, respectively, with a standard error of about ± 0.002 g cm^{-3} for each value. For comparison to amorphous acetone, the liquid state has $n_D = 1.356$ and $\rho = 0.784$ g cm^{-3} at 25 °C [9]. Diffraction studies give the density of crystalline acetone as 0.987 g cm^{-3} [10].

3.2. Infrared Spectra and Band Strengths

To check that our spectra were neither saturated nor resolution limited, IR spectra were first recorded for ice thicknesses up to 4 μm and resolutions up to 0.5 cm^{-1}. Since little change was found beyond 1 cm^{-1}, that resolution was used in most of our work.

Fig. 1 shows survey spectra of acetone deposited at 10 K to make an amorphous solid and at 125 K to make a crystalline one, the latter as indicated by the increase in splitting of peaks on going from (a) to (b) and the decrease in widths of several bands. Peak positions for the two traces are similar, but there are differences in relative intensities. Table 1 lists positions of selected IR peaks in our spectra of amorphous and crystalline acetone in Fig. 1, along with some literature results for comparison. Assignments to specific modes are taken from gas-phase studies [11] and are, of course, approximations for these solids. Mixing is expected as are factor-group splittings. Although crystalline acetone has little direct relevance to the study of extraterrestrial ices, recent work by our group has uncovered confusion in the literature involving IR spectra of solid N_2O, C_2H_2, C_2H_4, CH_4, CO_2, CH_3SH, and C_2H_5OH, all molecules of astrochemical interest, emphasizing the importance of having reference spectra for both non-crystalline and crystalline solids [6,8,12,13,14,15,16].

Figs. 2 and 3 have spectra for the same two ices as in Fig. 1, but traces (b) and (c) show the effect of warming the amorphous sample that was

Table 1
Positions of some acetone vibrations.

Mode ν	Approximate motion	Amorphous, 10 K IR[a]	Crystalline 125 K IR[a]	Solid 13 K IR[b]	Solid 77 K Raman[c]
ν_{13}	CH$_3$ asymm stretch	3002.0	3002.9	3001.8	3004.0
ν_1	CH$_3$ asymm stretch	3002.0	2999.0	3001.8	3004.0
ν_9	CH$_3$ asymm stretch	2967.4	2969.3	2967.0	2972.0
ν_{20}	CH$_3$ asymm stretch	2967.4	2969.3	2967.9	2972.0
ν_2	CH$_3$ symm stretch	2920.5	2921.5	2919.7	2920.0
ν_{14}	CH$_3$ symm stretch	2920.5	2918.4	2919.7	2920.0
ν_3	C=O stretch	1711.4	1715.2, 1708.1, 1704.8, 1698.8	1711.0	1697.0
ν_{21}	CH$_3$ asymm def	1441.6	1442.8, 1439.8	1441.9	1444.0
ν_{10}	CH$_3$ asymm def	–	1433.8	–	1431.0
ν_4	CH$_3$ asymm def	1418.9	1418.7	1419.1	1426.0
ν_{15}	CH$_3$ asymm def	–	1403.2	–	1408.0
ν_{16}	CH$_3$ symm def	1364.4	1360.9	1364.0	1366.0
ν_5	CH$_3$ symm def	1350.8	1350.3, 1346.8	1351.8	1351.0
ν_{17}	CCC asymm stretch	1228.9	1234.0	1229.5	1229.0
ν_{22}	CH$_3$ rock	1095.6	1098.5	1096.0	1098.0
ν_6	CH$_3$ rock	1071.4	1072.0[d]	1070.0	1072.0
ν_{18}	CH$_3$ rock	897.3	907.2	897.9	905.0
ν_{11}	CH$_3$ rock	871.0	873.4	872.3	872.0
ν_7	CCC symm stretch	791.2	793.9	791.1	796.0
ν_{19}	CO in-plane def	533.6	533.7	–	533.0
ν_8	CCC scissoring	–	–	–	497.0
ν_{23}	CO out-of-plane def	–	–	–	402.0
ν_{24}	Torsional	–	–	–	130.0
ν_{12}	Torsional	–	–	–	112.0

[a] This work; assignments at 1500–1400 cm^{-1} are somewhat uncertain.
[b] From Andrade et al. [4] arranged to correspond to modes (ν) in the first column, but with the authors' peak near 1035 cm^{-1} omitted.
[c] From Harris and Levin [28].
[d] Broad feature.