Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 283 (2022) 121738

Contents lists available at ScienceDirect

Spectrochimica Acta Part A:
Molecular and Biomolecular Spectroscopy

journal homepage: www.journals.elsevier.com/spectrochimica-acta-part-a-molecular-and-biomolecular-spectroscopy

Infrared intensities of methyl acetate, an interstellar compound - comparisons of three organic esters

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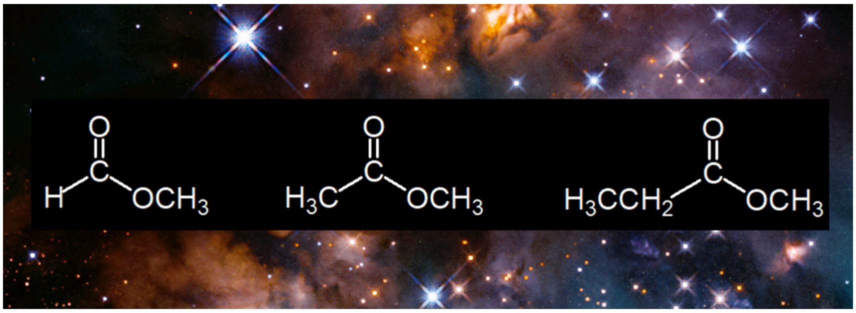
HIGHLIGHTS

- Transmission IR spectra of amorphous and crystalline methyl acetate are presented.
- Band intensities have been measured.
- Optical constants have been calculated.
- Spectra and optical constants are electronically available.
- Comparisons are made to spectra of methyl formate and methyl propionate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Astrochemistry – method
Laboratory – solid state
IR spectroscopy – ISM
Methyl acetate – Physical properties
Band strength and optical constants

ABSTRACT

The mid-infrared (IR) spectra of the simplest aliphatic esters have been studied in the past in the solid, liquid, and gas phases with an emphasis on vibrational frequencies and peak assignments. However, relatively little has been published on the IR intensities of the amorphous forms of these compounds. These IR intensities are of particular interest to the astrochemical community as they are needed to help quantify laboratory measurements of the formation and destruction of extraterrestrial molecules, including esters. Here we report and compare IR intensities of three organic esters: methyl formate, methyl acetate, and methyl propionate, all studied with the same equipment and procedures. Of these three esters, our main interest is with methyl acetate, for which little quantitative IR work is available. For each ester, we report apparent absorption coefficients and band strengths, and compare them to earlier work. We also have calculated the first IR optical constants for both amorphous and crystalline methyl acetate. We use our new results to measure vapor pressures and a sublimation enthalpy for methyl acetate and to comment on a radiation-chemical experiment with methyl acetate and how it can be better quantified.

1. Introduction

Of the roughly 200 molecules and ions identified in interstellar space, many are of sufficient complexity that a gas-phase synthesis seems impossible, due to low gas-phase densities and temperatures in interstellar space, leaving the solid phase as their source. Temperatures

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https://doi.org/10.1016/j.saa.2022.121738
Received 7 May 2022; Accepted 6 August 2022
Available online 10 August 2022
1386-1425/Published by Elsevier B.V.

are near 10 K in dark interstellar clouds composed of gas and refractory solids. Ices are present on these solids, with a composition that includes a number of fairly small, simple molecules, such as H_2O, CO_2, and CH_3OH. Exposure to ionizing radiation, both particulate (i.e., cosmic rays) and photonic (i.e., far-UV) induces reactions that generate more-complex molecules, which are released into the gas phase where they are identified [1].

Infrared (IR) spectroscopy has been invaluable in the study of extraterrestrial ices, both through astronomical observations and laboratory studies. In both cases, the two reference spectroscopic quantities of greatest need are spectral positions and IR intensities, such as band strengths or absorption coefficients for IR peaks. However, although the IR literature contains extensive results on spectral positions, peak assignments, and vibrational modes, quantitative results on intensities for many compounds in the solid state have either never been published or never independently verified. The centrality of such reference IR intensities for calculating abundances in astrochemical problems is well illustrated by discussions in both a recent and an older review of icy solids in extraterrestrial environments [2,3]. See also the older work of Hudgins et al. [4] or of d'Hendecourt and Allamandola [5].

In this paper we report new results on the mid-IR intensities of the three organic esters shown in Fig. 1, all being studied as amorphous solids as that is the form in which they are most likely found in interstellar ices. The first of these esters, methyl formate, has been detected in two different conformations in the gas phase in the interstellar medium [6,7]. The second ester in Fig. 1, methyl acetate, also has been observed in interstellar space [8], and the third is suspected [9]. In contrast, quantitative solid-phase studies of the formation and destruction of these esters are relatively scarce, hindered by the lack of quantitative laboratory data. Papers have been published with intensity measurements for methyl formate [10] and methyl propionate [11] ices, but not for methyl acetate. Here we report the first measurements of IR intensities of amorphous and crystalline methyl acetate, along with new results for the other two esters of Fig. 1. We combine the present work and recently published results for methyl acetate [12] to determine, for the first time, IR band strengths, absorption coefficients, and optical constants for methyl acetate ices. We also present vapor pressures and an enthalpy of sublimation for solid methyl acetate.

2. Experimental

All reagents were purchased from Sigma Aldrich (MilliporeSigma) and were used as received aside from vacuum-line transfers, degassing with liquid nitrogen, and storage at 3 °C before and after use. The laboratory equipment used and methods followed have been described in our previous papers [e.g., 13,14,15]. Briefly, ices were formed by vapor-phase deposition onto a pre-cooled substrate, either KBr or CsI, in the center of a high-vacuum chamber (pressure $\sim 10^{-8}$ Torr at 10 K). Amorphous ices resulted when the deposition temperature was near 10 K, but these ices crystallized on warming. Depositions at higher temperatures gave crystalline ices directly (vide infra). The deposition rates used were such as to give an increase in the thickness of each ice sample of a few micrometers per hour.

Interference fringes recorded from the substrate and sample during ice growth were used to determine ice thickness according to the method described by Groner et al. [16]. The relevant equation for ice thickness (h) is shown in (1).

$$h = \frac{N_{fr}\lambda}{2\sqrt{n^2 - sin^2\theta}} \tag{1}$$

where $\theta = 3.57 \pm 0.04^\circ$ is the angle between the incident beam from a laser ($\lambda = 670$ nm) and a line drawn perpendicular to the substrate and n is the ice's refractive index at 670 nm. For our experimental conditions, $N_{fr} = 4$ fringes corresponds to an ice thickness of about 1 μm. See our earlier papers for additional details and references [e.g., 10,11,12]. Equation (1) requires values of n at 670 nm for each compound studied. These were taken from recent measurements [12] in our laboratory and are given in Table 1, with standard errors in n_{670} of $\pm$ 0.005.

Infrared transmission spectra from 4000 to 400 cm^{-1} were recorded of methyl formate, methyl acetate, and methyl propionate at 16 K with a Mattson Polaris FTIR spectrometer at 2-cm^{-1} resolution and 100 scans per spectrum. These were recorded to compare spectra of the three esters and particularly to compare our methyl formate results with those in the literature. A few checks were made with 1-cm^{-1} resolution, but IR bands were sufficiently broad that little was gained by the added time needed to acquire the spectra at the higher resolution. In other words, our measurements were not resolution limited. Nevertheless, when we moved to our main interest, IR intensities of solid methyl acetate, for which few published IR spectra are available, we used a Thermo iS50 FTIR spectrometer at a resolution of 1 cm^{-1} and 200 scans per spectrum. Each spectrometer had a DTGS detector.

Infrared spectra were recorded for each solid at the temperature of the ice's growth and, with methyl acetate, after warming or cooling to a few other temperatures. However, our priority was not temperature-induced spectral changes, but spectra as a function of ice thickness. From the latter, we derived apparent absorption coefficients (α') of selected IR peaks and apparent strengths (A') of selected IR bands from ices having a range of thicknesses. Apparent absorption coefficients (α') were found using Beer's law and graphs of "ln(10) × peak height" as a function of ice thickness, their slope giving α' directly. See equation (2).

$$ln(10) \times (Absorbance\ of\ peak) = \alpha' h \tag{2}$$

The "ln(10)" term was needed to convert from absorbance to an optical-depth scale. Apparent band strengths (A') were found as described by Hollenberg and Dows [17] and as in our earlier papers [e.g., 13,14]. Selected IR bands were integrated, graphs of "ln(10) × band area" prepared, and their slopes used to derive A', according to equation (3).

Table 1
Physical properties of three amorphous esters[a].

Amorphous solid	T / K	n_{670}	ρ / g cm^{-3}	m / 10^{-22} g
methyl formate	15	1.317	0.926	0.9972
methyl acetate	15	1.309	0.832	1.230
methyl propionate	15	1.302	0.764	1.463

[a] Standard errors in n_{670} and ρ are ± 0.005 and 0.005 g cm^{-3}, respectively. See also Hudson et al. [12] for details of measurements.

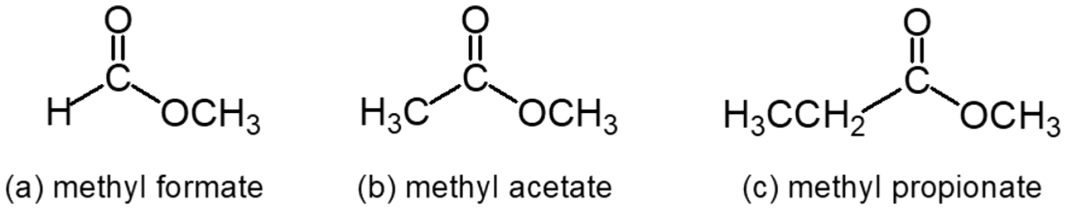


Fig. 1. Three organic methyl esters.

$$ln(10) \times \int_{band} (Absorbance) d\tilde{\nu} = (\rho_N A') h \tag{3}$$

The number density (ρ_N molecule cm^{-3}) of each amorphous ice sample was calculated from the mass densities of Table 1 (standard errors in ρ are ± 0.005 g cm^{-3}). Uncertainties in α' and A' are on the order of 5 %, and less for the stronger IR features. See Hudson et al. [11,12] for a discussion of errors and uncertainties. For the distinction between apparent and absolute absorption coefficients and band strengths, and the notations used, see Hudson et al. [18] and references therein.

In using equations (2) and (3), we studied between four and six ices in each case, with ice thicknesses corresponding to about 0.5 to 2.5 μm. Not every IR peak and band in every spectrum was measured, but rather features that seemed reasonably strong and free of extensive overlap, as such features will be those most useful to laboratory astrochemical work. By necessity, some regions examined correspond to more than one vibrational mode.

3. Results

Fig. 2 shows IR spectra of the three esters covered in this paper, with the spectra shown being for amorphous samples at 16 K and each being among our thicker ices so as to better show weaker spectral features. These three esters will be treated in the top-to-bottom order of Fig. 2.

3.1. Mid-infrared spectra of methyl formate

Intensities of IR bands of amorphous methyl formate have been reported by Modica and Palumbo [9], and provided a valuable way to check our methods and equipment. The uppermost trace of Fig. 2 shows an IR survey spectrum of methyl formate vapor deposited at 16 K, and Table 2 gives peak positions and ranges of IR features of amorphous methyl formate selected for intensity measurements. Warming the amorphous ice to 90–100 K resulted in its crystallization. Crystalline methyl formate also was produced by vapor-phase deposition at 115 K. Subsequent warming to about 130 K resulted in the ice's sublimation in about 5 min. Crystallization and sublimation times were longer for lower temperatures and shorter for higher ones.

Our methyl formate spectrum of Fig. 2 agrees qualitatively with that of Modica and Palumbo [10]. The last two columns of Table 2 present a quantitative comparison through band strengths. Given the difficulty of intensity measurements, the agreement is again good, within 10 %. See Fig. 3 for a graphical comparison. Differences can be attributed to the fact that the previous workers used an ice density obtained from the Lorentz-Lorenz equation and room-temperature liquid-phase data, which gave an ice density about 6 % smaller than our measured value. Also, no integration ranges were given for the band strengths reported [10]. However, the point we emphasize is that the lab-to-lab agreement is very good.

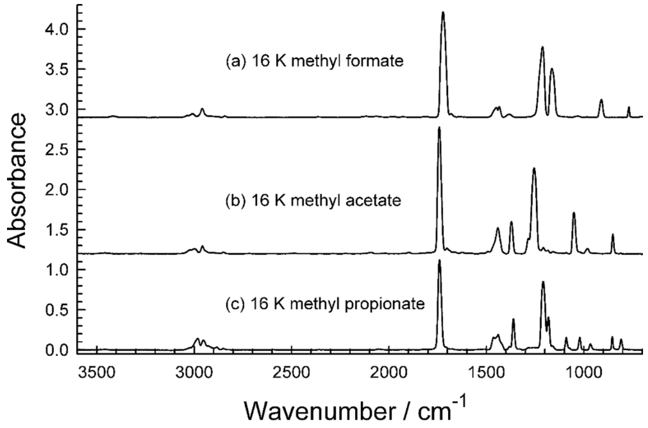


Fig. 2. Infrared survey spectra of amorphous (a) methyl formate, (b) methyl acetate, and (c) methyl propionate, all at 16 K. The thickness of the formate ice was about 2.0 μm, and the thickness of the acetate and propionate ices was about 2.5 μm. Ices were made and spectra were recorded at the temperatures indicated. Spectra are offset for clarity.

Table 2
Intensities of selected IR absorptions of amorphous methyl formate at 16 K.

Approximate description[a]	$\tilde{\nu}$/ cm^{-1}	α' / cm^{-1}	Integration range / cm^{-1}	A' / 10^{-18} cm $molecule^{-1}$	A' / 10^{-18} cm $molecule^{-1}$ - lit.[b]
CH_3 stretches	3008	476	3100–2800	6.44	—
H—C(O) stretch	2958	1211			
C=O stretch	1721	14,576	1770–1657	48.3	49.6
	1450	1361	1500–1412	5.69	5.58
CH_3 bendings	1434	1484			
	1382	334	1412–1350	0.981	—
HC–O stretch	1211	9733	1300–1186	31.4	29.3
CH_3 rocking	1164	6686	1186–1100	18.9	19.6
O–CH_3 stretch	910	2461	950–870	5.16	4.82
OCO bending	769	1406	785–745	1.31	1.25

[a] Descriptions from Wilmshurst [20]. See also Susi and Zell [28].
[b] From Modica and Palumbo [10]. No integration ranges were given.

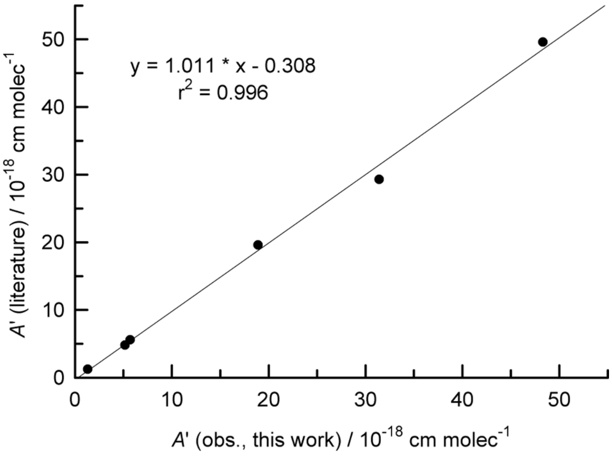


Fig. 3. Infrared band strengths of amorphous methyl formate near 16 K in this work compared to values from Modica and Palumbo [10].

Here we should note out that our spectra of methyl formate and the other esters of Fig. 1 showed significant overlap among the many IR features of each compound. Also, combination and overtone bands (e.g., ~3410 cm^{-1} overtone for the C=O stretch in methyl formate) gave rise to numerous small features among the fundamentals. These weaker peaks, along with the mixing of modes in the solid state, made definitive assignments difficult in some cases, as evidenced by some disagreements in the spectroscopic literature for these molecules. These small features are of little relevance for the astrochemical applications we envision and were, for the most part, ignored.

3.2. Mid-infrared spectra of methyl acetate

As with methyl formate, there have been several earlier studies of solid methyl acetate focusing on peak positions, peak assignments, and vibrational modes [e.g., [19–21]. However, we have not found laboratory measurements of IR intensities, either α' or A', for solid methyl acetate.

Vapor-phase deposition of methyl acetate at 10 K resulted in an amorphous ice that, on warming at a few degrees per minute, crystallized in less than a minute at 110 K. Holding a warmed sample overnight at 100 K also caused crystallization. Deposition at 115 K gave a crystalline sample with no need for warming. Survey spectra are shown in Figs. 2 and 4, with expansions shown in Figs. 5 and 6. To our knowledge, these are the first mid-IR transmission spectra of amorphous methyl acetate over this large a wavenumber range. Although our main interest in solid esters concerned their amorphous forms, having methyl acetate on hand we also took the opportunity of recording spectra of the crystalline material, which also are shown in Figs. 5 and 6.

Measurements of the heights of absorbance peaks and areas of absorbance bands of methyl acetate gave intensities α' and A', respectively, from Beer's Law plots. Representative graphs are shown in Fig. 7, with all such regression lines having correlation coefficients above 0.995. Tables 3 and 4 give peak positions and the results of intensity measurements (i.e., α' and A') for the amorphous and crystalline solids. The density $\rho = 1.197$ g cm^{-3} and refractive index, $n_{670} = 1.484$, we used to compute band strengths for crystalline methyl acetate are from Yarnall & Hudson [22].

As an application of our results for crystalline methyl acetate, we determined the vapor pressure of this solid at three temperatures using our band strengths and the method of Khanna et al. [23], and following the 1505–1400, 1400–1344, 1076–1000, and 1000–950 cm^{-1} regions, essentially the same as those in Table 4. Results were $p(135\text{ K}) = 8.07 \times 10^{-7}$ Torr, $p(140\text{ K}) = 3.92 \times 10^{-6}$ Torr, and $p(145\text{ K}) = 1.84 \times 10^{-5}$ Torr. A Clausius-Clapeyron plot with this data was linear (correlation coefficient = 0.999) with a slope that gave an enthalpy of sublimation of 51 kJ mol^{-1}, essentially the same as what we reported for methyl propionate [11]. A check on this result should be possible by, for example, the use of a quartz-crystal microbalance, work for the future [24].

Before leaving methyl acetate, we note that our spectra are consistent with that of the *cis* conformer, with no evidence of the less-abundant, higher-energy form in which the methyl group is *trans* to the carbonyl group. See Jones and Owen [25] and references therein for more information on these isomers. An isolated *cis*-methyl acetate molecule has, at best, C_s symmetry with $3N - 6 = 3(11) - 6 = 27$ fundamental vibrations. No attempt was made to observe each of these as again our focus was on intensity determinations for the strongest IR features.

3.3. Mid-infrared optical constants of methyl acetate

Our spectra of methyl acetate ices of different thickness also were used to calculate IR optical constants $n(\tilde{\nu})$ and $k(\tilde{\nu})$. The iterative procedure adopted is described in previous papers from our group, and involves IR spectra of ices of known thickness, a reference refractive index (see Table 1), and a Kramers-Kronig routine. The method is described in Gerakines & Hudson (2020), with the computer code available in two formats [26]. We emphasize that our method is fast, accurate, flexible, robust, and open-source. Fig. 8 shows the results for amorphous and crystalline methyl acetate, with these $n(\tilde{\nu})$ and $k(\tilde{\nu})$ values available on our group's website at https://science.gsfc.nasa.gov/691/cosmicice/constants.html. These are the first optical constants published for methyl acetate ices.

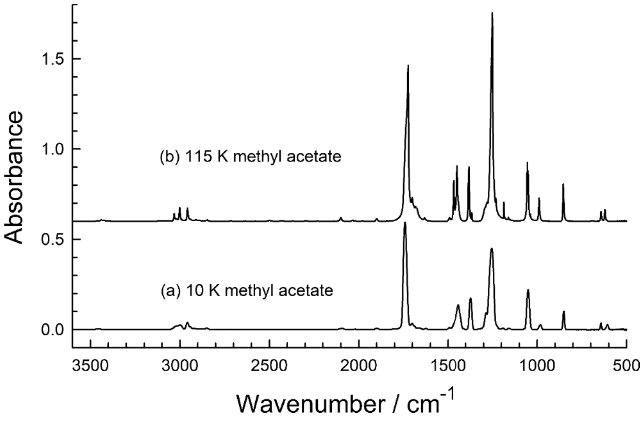


Fig. 4. Infrared survey spectra of (a) amorphous and (b) crystalline methyl acetate at 10 and 115 K, respectively. The thickness of the ice in (a) was 1.02 µm and the thickness of the ice in (b) was 0.926 µm. Each ice was made at the temperature indicated. Spectra are offset vertically for clarity.

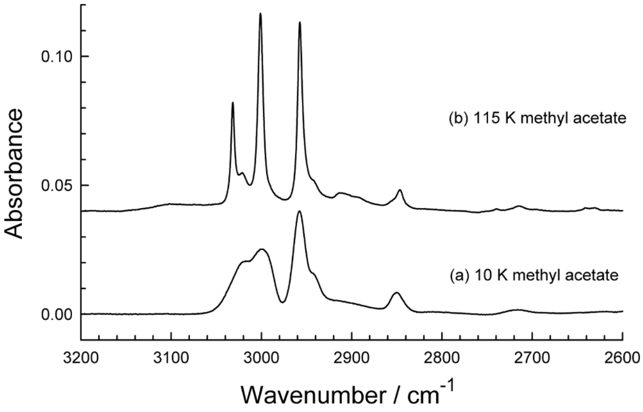


Fig. 5. Spectra of (a) amorphous and (b) crystalline methyl acetate in the C—H stretching region. The thickness of the ice in (a) was 1.02 µm and the thickness of the ice in (b) was 0.926 µm. Each ice was made at the temperature indicated. Spectra are offset vertically for clarity.

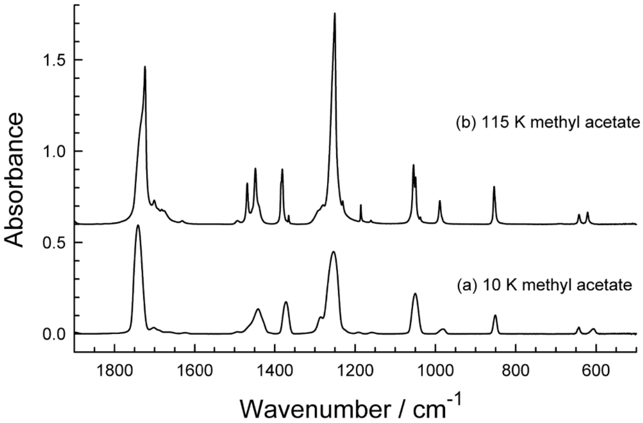


Fig. 6. Spectra of (a) amorphous and (b) crystalline methyl acetate between 1900 and 500 cm^{-1}. The thickness of the ice in (a) was 1.02 µm and the thickness of the ice in (b) was 0.926 µm. Each ice was made at the temperature indicated. Spectra are offset vertically for clarity.

3.4. Mid-infrared spectra of methyl propionate

The bottom trace of Fig. 2 shows a survey spectrum of methyl propionate, on which we already have published [11]. In the interest of uniformity, we have used our new values of n_{670} and ρ for amorphous methyl propionate, given in Table 1, to recalculate α' and A' for that solid, and the results are in Table 5. The values there for α' and A' are about 1.5 % and 6.7 %, respectively, smaller than the old values. Assignments are not given in this table as in most cases vibrational motions of methyl propionate are so complex as to hinder simple qualitative descriptions. Interested readers should consult the paper of Moravie and Corset for more information [27].

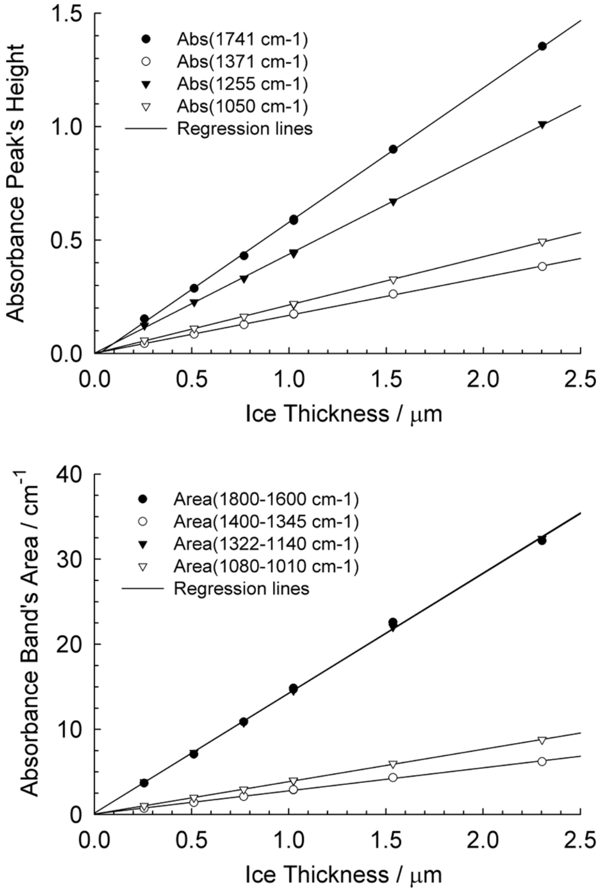


Fig. 7. Representative Beer's Law plots for the determination of apparent absorption coefficients (α') and band strengths (A') of amorphous methyl acetate at 10 K. Note that in the bottom graph two of the regression lines are almost superimposed.

Table 3
Intensities of selected IR absorptions of amorphous methyl acetate at 10 K.

Approximate description[a]	$\tilde{\nu}$ / cm^{-1}	α' / cm^{-1}	Integration range / cm^{-1}	A' / 10^{-18} cm molecule^{-1}
CH_3 stretches	2999	539	3070–2869	11.3
CH_3 stretches	2958	849		
C═O stretch	1741	13,600	1790–1643	48.0
CH_3 bendings	1441	2980	1510–1400	13.7
C–CH_3 deformation	1372	3840	1400–1350	9.21
H_3CC–O stretch	1254	10,000	1318–1208	47.9
C–CH_3 stretch	1050	4900	1080–1025	13.0
C–CH_3 rocking	981	560	1005–965	1.42
O–CH_3 stretch	851	2240	870–830	3.48
OCO deformation	643	743	655–630	0.938
OCO deformation	607	586	630–591	1.22

[a] Approximate descriptions are taken from the work Wilmshurst [19], George et al. [20], and Maes [21].

4. Discussion

4.1. Infrared spectra

As already stated, the IR spectra of each of our three organic esters has been studied in the past, usually with an emphasis on peak assignments or vibrational modes. For methyl formate, Susi and Zell [28] assigned peaks for both gas- and liquid-phase spectra, followed by a normal coordinate analysis by Susi and Scherer [29], but only qualitative descriptions of IR intensities. Katon and Ranieri [30] also published IR spectra, but again no numerical intensities. We already have pointed out that the best comparison of our work is to the IR measurements of Modica and Palumbo [10] and that there is good agreement between their results and ours.

Table 4
Intensities of selected IR absorptions of crystalline methyl acetate at 115 K.

Approximate description[a]	$\tilde{\nu}$ / cm^{-1}	α' / cm^{-1}	Integration range / cm^{-1}	A' / 10^{-18} cm molecule^{-1}
CH_3 stretches	3001	1900	3050–2830	5.15
CH_3 stretches	2957	1800		
C═O stretch	1723	23,200	1800–1600	58.9
CH_3 bendings	1448	7310	1510–1405	14.8
C–CH_3 deformation	1381	6880	1405–1345	6.75
H_3CC–O stretch	1251	25,800	1330–1110	62.3
C–CH_3 stretch	1054	7430	1100–1010	9.14
C–CH_3 rocking	989	2950	1010–960	2.37
O–CH_3 stretch	854	4970	870–815	3.90
OCO deformation	642	1350	667–595	2.17
OCO deformation	621	1580		

[a] Approximate descriptions are taken from the work Wilmshurst [19], George et al. [20], and Maes [21].

Our primary interest in the present paper is methyl acetate, which appears to have first been studied by Coblentz [31], followed by, for example, Thompson and Torkington [32], Nolin and Jones [33], Wilmshurst [19], and others up to the present, including matrix-isolation studies by Fausto and Teixeira-Dias [34] and Blom and Günthard [35]. George et al. [20] list peak positions for crystalline methyl acetate that differ from ours by only 1–2 cm^{-1}, but again no numerical intensities were given. Francis [36] reported intensities for room-temperature liquids, but not for solids. However, since amorphous solids can be considered "frozen liquids", in Table 6 **and** Fig. 9 we compare our A' values of amorphous methyl acetate with the published values of Francis [36] for five IR regions. Given that the published values involved different integration ranges from our own, and that some ranges were not stated, the agreement and the trend in the data seem reasonable. Comparisons of our band strengths for crystalline methyl acetate are even more difficult, as no measurements were found in the literature.

Several IR papers on solid methyl acetate have appeared in recent years with an eye towards astrochemical applications, our own area of interest. The paper of Sivaraman et al. [37] gives peak positions for amorphous and crystalline methyl acetate at several temperatures, but no intensity measurements were reported. Moreover, the spectra presented were recorded by reflection from a gold substrate (angle not given), which can render intensities of limited value for comparisons. For example, the relative intensities of those authors' spectral peaks disagree strongly with our own work in Figs. 4 - 6 and with the crystalline ice spectrum of George et al. [20]. A later paper by Sivaraman et al. [38] did present transmission IR data, but the spectra had significant gaps, such as the 2050–1195 cm^{-1} region, which includes the strongest IR peaks in the spectrum. No absolute intensities were provided, and neither ice thicknesses nor spectral resolution were given.

Two recent publications reported calculations of methyl acetate's IR peak positions and intensities. However, in Das et al. [39] the calculated spectra are presented on such a small scale, and with overlapping lines and colors, as to make quantitative comparisons difficult. It also is not clear which peaks are most appropriate for comparison to the laboratory data. More promising are the density-functional calculations for crystalline *cis*-methyl acetate reported by Narayanan et al. [40], although it is unfortunate that intensity results in that paper were given only as relative values, scaled to the strongest IR feature, and not as absolute intensities. Qualitatively, the intensities of the calculated spectrum of those authors' Fig. 4 are in poor agreement with the laboratory spectrum presented for comparison, particularly from about 1750 to 750 cm^{-1}. The reason for the disagreement appears to be that the comparison

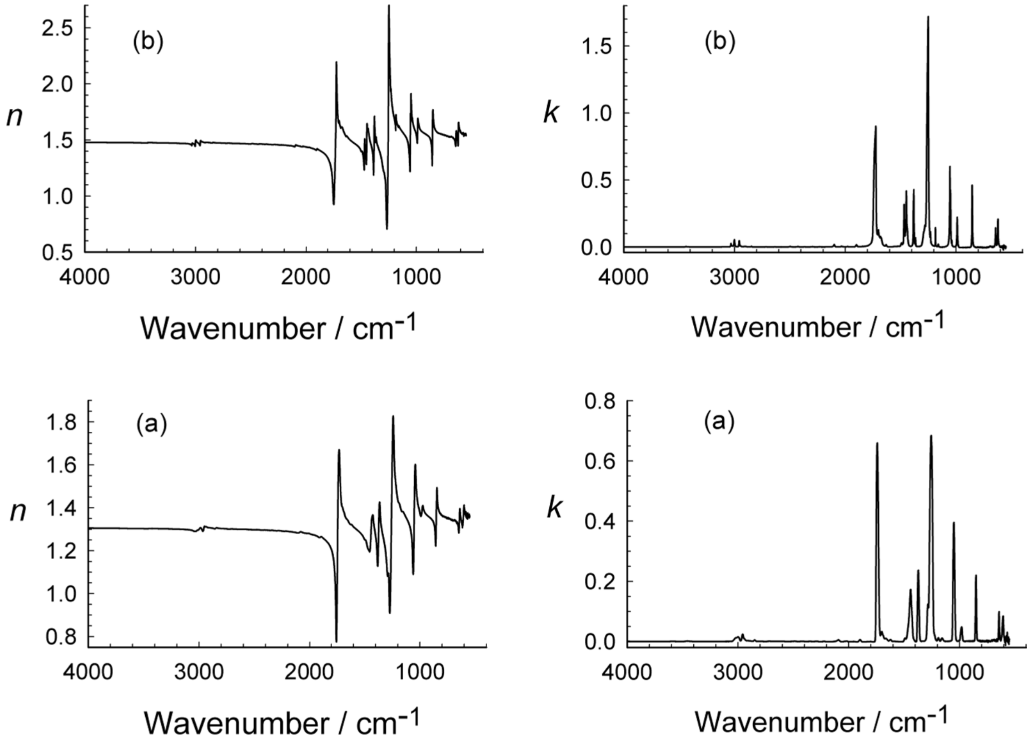


Fig. 8. Infrared optical constants of (a) 10 K amorphous and (b) 115 K crystalline methyl acetate.

Table 5
Intensities of selected IR absorptions of amorphous methyl propionate at 16 K[a].

$\tilde{\nu}$ / cm^{-1}	α' / cm^{-1}	Integration range / cm^{-1}	A' / 10^{-18} cm molecule^{-1}
2981	1283	3100–2750	20.3
2953	1078		
1741	9808	1780–1660	41.8
1439	1767	1490–1400	15.3
1361	3412	1400–1313	11.4
1208	7595	1313–1135	51.0
1181	3405		
1090	1368	1130–1050	4.0
1021	1334	1050–990	3.4
966	639	990–930	1.7
854	1340	870–830	2.5
808	1118	830–780	2.8

[a] For additional details, such as assignments, see Hudson and Mullikin [11] and references therein.

Table 6
Intensities of selected IR regions of amorphous ice and liquid methyl acetate[a].

Region / cm^{-1}	Approximate description[b]	Amorphous Ice A' / 10^{-18} cm molecule^{-1}	Liquid A' / 10^{-18} cm molecule^{-1}
3070–2869	CH_3 stretches	11.3	10.8
1790–1643	C=O stretch	48.0	42.7
1510–1400	CH_3 bendings	13.7	11.1
1400–1350	C-CH_3 deformation	9.21	8.41
1318–1208	H_3CC-O stretch	47.9	46.4

[a] Ice A' values are from this work and were measured at 10 K. Liquid A' values were measured at room temperatures [36].

[b] Approximate descriptions are taken from the work Wilmshurst [19], George et al. [20], and Maes [21].

spectra are the same as those in Sivaraman et al. [37], which were obtained in a reflection mode that can distort intensities. Our own spectra, such as in Figs. 4 - 6, are in much better agreement with the calculated one, ours being dominated by two intense peaks near 1730 and 1250 cm^{-1}, similar to the dominance of the calculated spectrum by two peaks near those same regions [40].

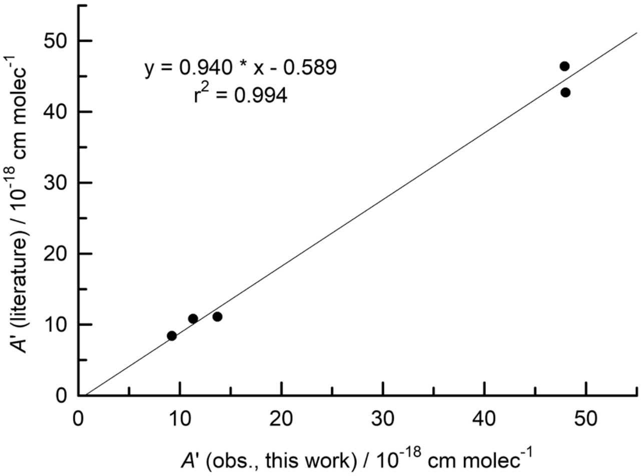


Fig. 9. Infrared band strengths measured for amorphous methyl acetate at 10 K compared to those of the room-temperature liquid [36].

4.2. Band strength comparisons

The two most prominent IR bands of the esters in Fig. 1 correspond to the carbonyl (C=O) and C—O (C-OCH_3) bond stretches. Our measurements gave band strengths (A') for the carbonyl (C=O) features as 4.83 × 10^{-17}, 4.80 × 10^{-17}, and 4.18 × 10^{-17} cm molecule^{-1} for the formate, acetate, and propionate, respectively. This is not a particularly large range, and no significant variation was expected. Similarly, for the C—O bond stretch (C-OCH_3) our A' values are 3.14 × 10^{-17}, 6.23 × 10^{-17}, and 5.10 × 10^{-17} cm molecule^{-1} for the formate, acetate, and propionate, respectively, again not a large variation. Liquid-phase comparisons are hard to find, but the similarity of C=O and C-OCH_3 band strengths for our acetate and propionate resemble what was reported for the liquid phase by Francis [36]. Data for liquid methyl formate were not reported by that author. Comparisons of solid methyl acetate's IR band strengths to those of its isomers ethyl formate and propionic acid would be interesting, but we are unaware of any such measurements for either of those two compounds. Finally, the results reported in the present paper may serve as benchmarks for calculating IR band strengths in amorphous ices with modern computational methods.

4.3. Radiation chemistry and methyl acetate decomposition

One motivator for this study was our interest in the stability and decomposition of methyl acetate and related organic compounds in the solid state in extraterrestrial environments. We recently have examined the radiation-induced decomposition of compounds I – III in Fig. 10, and in each case we found that CO_2 was a radiation product. The solid-phase radiolysis of compound IV, methyl acetate, has been studied, and CO_2 was reported as a reaction product detected by IR spectroscopy [38]. The earlier study did not state the IR path length through the sample, but it can be estimated from our IR intensity results of Table 4. From the authors' Fig. 3(a) and the IR peak near 1050 cm^{-1}, we estimate the path length to be ~ 0.75 μm by using equation (2) above and α'(1050 cm^{-1}) in our Table 4. The ice sample's thickness will differ from 0.75 μm if the incident IR beam was not perpendicular to the substrate on which the ice was formed. We have digitized and integrated the published IR spectra and calculated that the loss of methyl acetate from the electron irradiation was about 1.4×10^{17} molecules cm^{-2}. The amount of CO_2 produced is more difficult to estimate, but using the band strength of Gerakines and Hudson [41], we calculated that the CO_2 column density rose by about 2.3×10^{16} molecules cm^{-2} due to the irradiation, for a conversion (yield) of 16 %, a value that depends strongly on the choice of A'(2340 cm^{-1}) for CO_2.

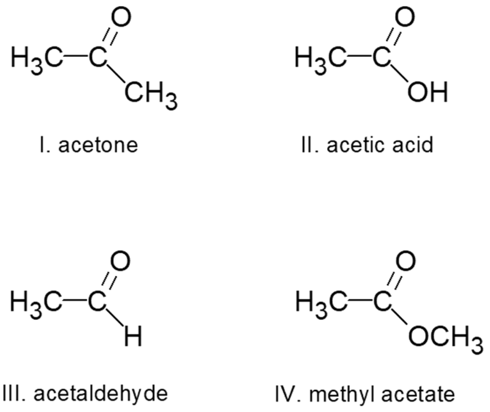
4.4. Other work

Our three esters are not expected to have high abundances in extraterrestrial ices, and so the detection and identification of these molecules in the solid state by IR astronomers will be difficult. This suggests that the main use of our work will be by laboratory astrochemists, such as in the application of our α' and A' values to measure ice thicknesses. Another application would be the determination of methyl acetate content when preparing multi-component ice mixtures, recognizing that interstellar and planetary ices are dominated by H_2O and other compounds. See our recent work on H_2O + HCN ices for an example [42]. With care, our results on esters also could be used to calculate peak or band intensities in both near- and far-IR spectra by taking appropriate ratios between our mid-IR α' and A' and spectral features in those two regions.

Another possibility for the future concerns investigations of the low-temperature formation of methyl acetate in extraterrestrial ices. The classic Fischer esterification, involving an alcohol and a carboxylic acid, with a mineral-acid catalyst, comes to mind [43]. This is all the more intriguing as methyl acetate precursors methanol and acetic acid are known interstellar molecules, with ionizing radiation in the form of cosmic rays able to produce acids such as H_2O^+ and H_3O^+ in water ices. The IR positions and intensities reported here for methyl acetate would be of value in identifying and quantifying that ester in irradiated CH_3OH + CH_3COOH ice mixtures. See Neill et al. [44] for an examination of esterification in the gas-phase of the interstellar medium.

5. Summary and conclusions

Here we have reported IR intensity measurements for three amorphous methyl esters, both absorption coefficients and band strengths, with an emphasis on methyl acetate. We also have presented transmission mid-IR spectra of amorphous methyl acetate over a larger wavenumber range than heretofore available, and have examined crystalline methyl acetate as well. Optical constants have been calculated for both forms of the compound. Qualitative and quantitative comparisons have been made to previous work. Expectations for the decomposition of methyl acetate in an extraterrestrial ice have been addressed, and some future work and applications are described.


I. acetone

II. acetic acid

III. acetaldehyde

IV. methyl acetate

Fig. 10. Four carbonyl-containing componds. Each exists in interstellar space.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Support from the NASA Astrobiology Institute through funding awarded to the Goddard Center for Astrobiology under proposal 13-13NAI7-0032 is acknowledged. Support also was received from NASA's Planetary Science Division Internal Scientist Funding Program through the Fundamental Laboratory Research (FLaRe) work package at the NASA Goddard Space Flight Center. Ella Mullikin (Wellesley College) contributed to the early stages of this work. YYY was supported by an appointment to the NASA Postdoctoral Program at the NASA Goddard Space Flight Center, administered by Universities Space Research Association under contract with NASA.

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