



Testing Densities and Refractive Indices of Extraterrestrial Ice Components Using Molecular Structures—Organic Compounds and Molar Refractions

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Abstract

The use of infrared spectra to determine molecular abundances of icy astronomical objects and to study their chemistry requires laboratory measurements of reference spectra and related quantities, such as the index of refraction (n) and density (ρ) of candidate ices. Here we present new n and ρ measurements on ices involving over 30 C-, H-, and O-containing compounds, both acyclic and cyclic, representing seven chemical families. We examine the results in a way that is rare in the astrochemical literature, namely one in which data from an ice formed from molecules of a particular chemical family are compared to measurements on another member of the same family, such as of a homologous series or a pair of isomers. Apart from the intrinsic usefulness of the n and ρ data, a structure-based comparison can help establish trends and identify possibly spurious results. As liquid-phase data sometimes are used in low-temperature astrochemical work in the absence of solid-phase measurements, we compare our new ice results to those for the corresponding room-temperature liquids. We emphasize the use of our n and ρ data to compute the molar refraction (R_M) for each of our ices, and how the resulting R_M values compare to those expected from molecular structures. The use of calculated R_M values and measured n values to calculate ice densities, in the absence of direct measurements, is also addressed.

Unified Astronomy Thesaurus concepts: [Astrochemistry \(75\)](#); [Laboratory astrophysics \(2004\)](#); [Molecular spectroscopy \(2095\)](#)

1. Introduction and Background to Measurements

Laboratory-based publications on astrochemically relevant ice molecules are usually focused on either a single or a few chemical compounds, and with an emphasis on the influence of physical parameters or conditions under the control of the laboratory scientist. Although this approach has provided considerable insight into a variety of astronomical environments, it can lead to the neglect of the rich connections that chemists have established among, for example, members of a homologous series or pairs of isomers. More specifically, one sometimes finds that various molecules are approached as isolated entities with few connections to related species, leading to a lost opportunity for the testing of new results in terms of chemical properties and molecular structures. In short, there is a danger that each new chemical system studied can become an island of research, separate from other work.

In this paper we adopt a broad approach to a problem related to laboratory measurements on compounds relevant to low-temperature interstellar and planetary chemistry. Here, we address the values and consistency of density (ρ) and refractive index (n) data needed to quantify and interpret the infrared (IR) spectra of icy extraterrestrial objects. We present n and ρ measurements on over 30 organic compounds, over 20 for the first time, data available for immediate use. For this work we adopt a different approach to test our results than is commonly used, and we then apply it to our chosen compounds, all examined with the same equipment and methods.

Even a cursory survey of the astrochemical literature will reveal a significant need for the type of measurements we are reporting. The majority of laboratory IR spectroscopic work to study ices over the past 40 yr has involved molecular

abundances in some way. Studies to arrive at optical constants and band strengths for ices sometimes were forced to use room-temperature n and ρ values simply because nothing else was available at the time (Hudgins et al. 1993). Investigations into the radiation chemistry and photochemistry of ices were forced either to do the same or to use gas-phase laboratory or computational results to quantify lab work (Öberg et al. 2009; de Barros et al. 2015; Bergner et al. 2019). A recent investigation of reductions of unsaturated alcohols and aldehydes was faced with the same challenge in trying to determine reaction yields, employing an indirect method to obtain band strengths (Jonusas et al. 2017). A laboratory examination of several organics relevant to future searches with the *James Webb Space Telescope* encountered similar difficulties (Terwisscha van Scheltinga et al. 2018). In fact, it still appears to be more common to find lab studies that need n and ρ values to determine ice sample thicknesses to convert band intensities into column densities, but cannot find them, than to encounter the opposite situation. Even for the abundant interstellar ice methanol (CH₃OH), it is only recently that direct measurements of n , ρ , and IR band strengths have been reported, nearly 30 yr after solid methanol was identified in the interstellar medium (ISM; Allamandola et al. 1992; Luna et al. 2018).

With the preceding in mind, the overarching purpose of our work is to provide data for quantitative studies of molecular abundances in cold (10–200 K) extraterrestrial environments using IR spectroscopy. Infrared spectra of molecular clouds in the ISM display IR absorbances on top of a blackbody continuum. After the latter is subtracted from the observational data, molecular abundances, expressed as column densities N ,

can be calculated from the residual IR bands according to

$$N = \frac{\int_{\text{band}} \tau d\tilde{\nu}}{A'} \quad (1)$$

where τ is the optical depth of an IR feature of interest and A' is the band's intrinsic intensity determined from laboratory measurements (*vide infra*). For spectra of ices on objects in the solar system, it is more common to record their IR spectra and then use combinations of reference spectra of various suspected or known ice components to fit the data. To compute such spectra, optical constants of the reference compounds are required, which again are obtained from lab measurements. What is needed in all cases are laboratory IR spectra of ices of known thickness.

Given these long-recognized needs, it is somewhat surprising that accurate determinations of IR band strengths of icy solids remain relatively scarce. One obstacle is shown by rearranging Equation (1) to give the following:

$$A' = \frac{\int_{\text{band}} \tau d\tilde{\nu}}{N} \quad (2)$$

This equation shows that an accurate laboratory measurement of A' for an ice requires (i) a reference spectrum, from which the integral of an IR band is determined, and (ii) the sample's column density (N), which typically is found from the ice's thickness and density.

Perhaps the most common and direct way that laboratory astrochemists measure the thickness of an ice sample is by using interference fringes. In our own case, the thickness (h) of an ice is found by counting the number of such fringes (N_{fr}) formed by a laser of wavelength λ incident on an ice during its growth, the laser's light being directed at an angle θ from a line perpendicular to the ice's surface. Equation (3) is used, where n is the ice's index of refraction at λ .

$$h = \frac{N_{\text{fr}} \lambda}{2\sqrt{n^2 - \sin^2 \theta}} \quad (3)$$

Obviously, n is needed before this method can be used to calculate an ice's thickness. Although in principle n can be found with fringe-intensity measurements using a single laser, in practice the method requires photometric measurements and a knowledge of the optical constants of the substrate, which are rarely known at the temperature of the experiment. Therefore, our preferred method for determining n is two-laser interferometry, which requires only the measurement of time and for which substrate optical properties are not needed. After n values are determined at the temperature of interest, ice thickness follows from the previous equation. See Heavens (2011), Tempelmeyer & Mills (1968), and Groner et al. (1973) for more information.

To calculate IR band strengths from spectra, Equation (4) from Hollenberg & Dows (1961) is used.

$$\int_{\text{band}} (\text{Absorbance}) d\tilde{\nu} = \left(\frac{\rho_N A'}{2.303} \right) h. \quad (4)$$

The quantity ρ_N is the ice sample's number density (molecules cm^{-3}), found from a measured mass density ρ and $\rho_N = \rho (N_A/M)$, where N_A is Avogadro's constant and M is the molar

mass (g mole^{-1}) of the compound being studied. If θ is small, then the two previous equations can be combined to give

$$A' = \left(\frac{2M}{N_{\text{fr}} \lambda N_A} \right) \left(\frac{n}{\rho} \right) (2.303) \int_{\text{band}} (\text{Absorbance}) d\tilde{\nu} \quad (5)$$

noting that $\tau = (2.303) (\text{Absorbance})$ converts the absorbance scale of commercial IR spectrometers to an optical depth (τ) scale.

Equation (5) shows that both n and ρ are needed to obtain an IR band strength (A') of an icy solid. Also, a propagation-of-error approach implies that errors in n and ρ combine to raise the uncertainty in A' . To aid in determinations of A' and to reduce the error involved, we report new measurements of both n and ρ , focusing on classes of organic molecules containing carbon, hydrogen, and oxygen. Our results constitute reference data for future laboratory studies that require ice thicknesses to be measured and will aid in the determination of IR band strengths and optical constants for astronomical observations. To check our measurements, we have used a quantity that involves both n and ρ . Specifically, the Lorentz-Lorenz equation was placed on a per mole basis and used to calculate the molar refraction, R_M , of each of our ices. See Equation (6).

$$R_M = \left(\frac{M}{\rho} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right). \quad (6)$$

Molar refractions have the virtue of being approximately additive for a wide variety of compounds, which allows for checking among a series of measurements on ices made from members of a homologous series, such as acetaldehyde (HC(O)CH_3), propionaldehyde ($\text{HC(O)CH}_2\text{CH}_3$), and butyraldehyde ($\text{HC(O)CH}_2\text{CH}_2\text{CH}_3$). Also, extensive n and ρ data are available for the liquids corresponding to our ices, so that comparisons between liquid and ice phase results are straightforward, although seldom if ever published. Molar refractions of isomers, such as 1- and 2-propanol, should be similar, which is yet another way we check our results. Finally, we compare our measured molar refractions to those predicted by a bond-additivity method.

An important goal of our work is to show the value of searching for consistency among laboratory measurements by paying explicit attention to molecular structure. No particular claim is made for novelty in this approach, but it has received little or no application within the astrochemistry community (Hudson & Coleman 2019a). Most studies to date have aimed to document variations in n and ρ by recording data as a function of temperature, concentration, or method of ice preparation for one- or two-component ices (e.g., Satorre et al. 2008; Loeffler et al. 2016). However, there is no a priori trend with which to test such results, which is not the case with the structure-based method used in this paper.

2. Laboratory Methods

The methods and equipment used are described in our recent papers (e.g., Loeffler et al. 2016; Hudson et al. 2017), so only a summary is given here.

Measurements of n and ρ were carried out in a UHV chamber ($P_{\text{min}} \sim 10^{-10}$ Torr) interfaced to a Thermo iS50 infrared spectrometer, the latter being used to check that ices were amorphous. To make ices, room-temperature vapors or gases were condensed onto a metal (gold) substrate at 15 K

Table 1
Densities of Five Crystalline Solids

Compound	T/K	$\rho/\text{g cm}^{-3}$	Reference
cyclopropane	65	0.916	This work ^a
	100	0.913	Nijveldt & Vos (1988)
acetone	125	0.999	Hudson et al. (2018)
	150	0.987	Allan et al. (1999)
methanol	120	1.02	This work ^a
	160	1.015	Torrie et al. (2002)
nitrous oxide	70	1.594	Hudson (2017)
	~80	1.56	de Smedt & Keesom (1924) ^b
carbon dioxide	70	1.68	Loeffler et al. (2016)
	~80	1.64	de Smedt & Keesom (1924) ^b

Notes.

^a Uncertainties for cyclopropane and methanol are 0.005 and 0.01 g cm^{-3} respectively.

^b The authors reported that the measurements were made at the temperature of liquid air.

within our UHV chamber at a rate that gave an increase in the resulting ice's thickness of about $1.5 \mu\text{m hr}^{-1}$, and with a disperser to aid in forming a uniform ice sample (Loeffler et al. 2016). During deposition, interference fringes from two lasers ($\lambda = 670 \text{ nm}$) at incident angles of $3^\circ.57 \pm 0^\circ.04$ and $53^\circ.57 \pm 0^\circ.24$ were recorded from the growing sample so that the ice's index of refraction could be determined. The 15 K metal substrate onto which ices were grown was the gold surface of an INFICON quartz-crystal microbalance, which was used to determine ice densities (Lu & Lewis 1972). Our methods for determining n and ρ resemble those of Satorre et al. (2008).

Measurements were made in triplicate, and in some cases more than three times, to reduce standard errors in n and ρ to ± 0.005 and $\pm 0.005 \text{ g cm}^{-3}$, respectively. Additional measurements and more-advanced methods for analyzing the data might improve the accuracy and precision of our results, but we do not expect substantial changes. In this paper, n is given to three decimal places, but rounding to two probably should be done in most cases, and to one decimal place for R_M values.

Few measurements of the type we are reporting for ices have been published, so a way was sought to check the experimental procedure and equipment used. Several of the compounds examined have been the subject of X-ray diffraction studies in which densities were measured for crystalline samples. Table 1 gives literature values for the densities of five crystalline solids along with new measurements reported here and some taken from our recent papers. Figure 1 compares the results graphically, and a high correlation coefficient is found.

Liquid-phase data used in this paper were taken from standard compilations such as Weast (1980) and Braker & Mossman (1971), and checked against data from our chemical supplier (Sigma Aldrich).

3. Results

For this study, we focused on four families of C-, H-, and O-containing organic molecules, aldehydes, ketones, esters, and alcohols, members of which are found in both interstellar and cometary environments. Most of the compounds examined have only one source of unsaturation, such as a carbon–oxygen double bond (C=O, carbonyl group) or a three-membered ring. One molecule has a carbon–carbon double bond and one has a

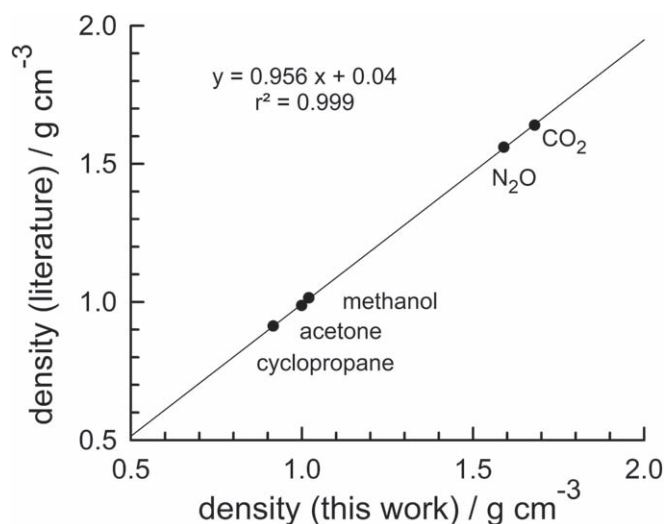


Figure 1. Comparison of densities of five crystalline ices. All values are taken from Table 1.

carbon–carbon triple bond. Although many of the compounds selected for study are known to be extraterrestrial, others are not and were chosen specifically for their value in comparing to laboratory results on interstellar and solar system molecules and the possibility that the compounds selected might later be found to be extraterrestrial. Two acyclic organic acids also were examined, as were two acyclic ethers, two cyclic ethers, and one organic diester. Future measurements are envisioned that will include N- and S-containing organic molecules.

Figures 2 and 3 show the molecules studied, with the drawings emphasizing the connectivity of the atoms as opposed to three-dimensional structures. These molecules are organized into seven categories, which we now address:

Aldehydes—Three acyclic aldehydes were examined, acetaldehyde (ethanal), propionaldehyde (propanal), and butyraldehyde (butanal), as well as one cyclic aldehyde, cyclopropanecarboxaldehyde. The first two named are known to be present in the interstellar medium (Fourikis et al. 1974; Hollis et al. 2004).

Ketones—Three acyclic ketones were studied, acetone (propanone), methylethyl ketone (butanone), and 3-pentanone, with the first being both interstellar and cometary (Combes et al. 1987; Snyder et al. 2002). Solid acetone is the only ice of these three for which n and ρ results have been published (Hudson et al. 2018). One cyclic ketone was studied.

Esters—Three methyl esters and two ethyl esters were examined, along with one cyclic ester. Of these six molecules, methyl formate, methyl acetate, and ethyl formate are known to exist in the ISM (Brown et al. 1975; Belloche et al. 2009; Tercero et al. 2013). Comparison data from other laboratories were found only for methyl formate (Modica & Palumbo 2010).

Alcohols—Of the nine alcohols studied, methanol (CH_3OH) has received by far the most attention in the past, being both a gas-phase cometary and interstellar molecule, as well as a major component of interstellar ices (Ball et al. 1970; Bockelée-Morvan et al. 1991; Allamandola et al. 1992). Much less laboratory work has been done with solid ethanol, and even less with the other alcohols in Figure 2. Two of the compounds shown, 2-propanol and 2-butanol, are secondary alcohols chosen for comparison to primary alcohols. Other than

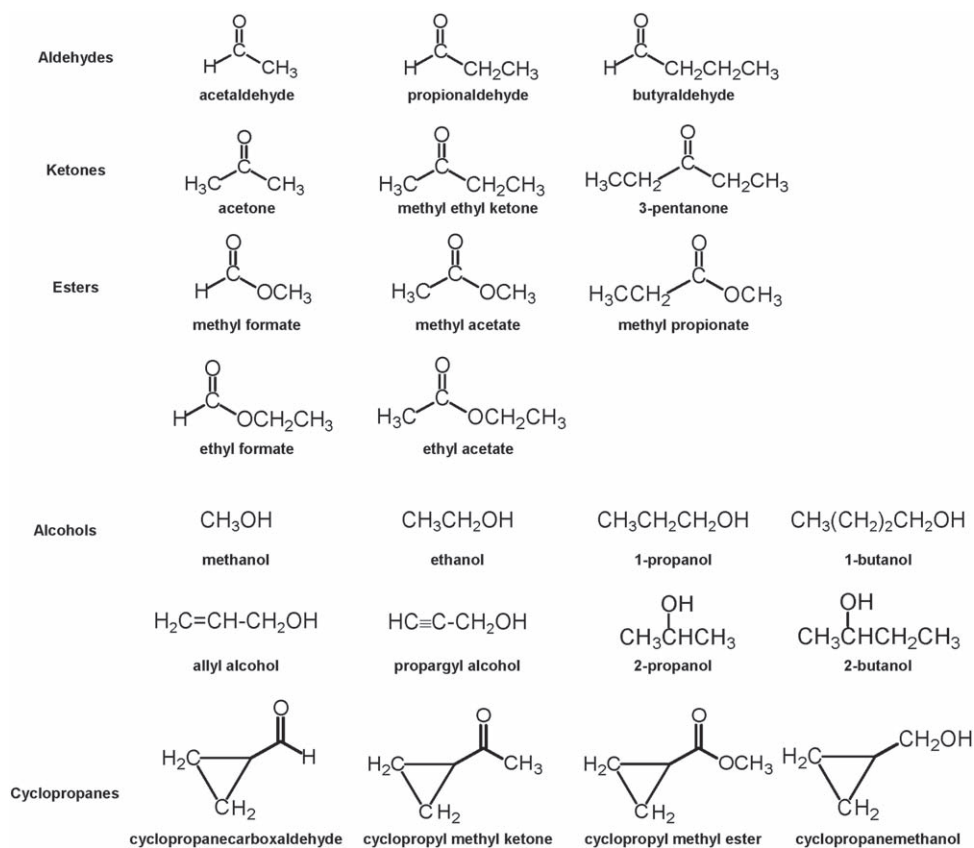


Figure 2. Simplified drawings of molecules examined in this work. Note that each of the four cyclopropanes at the bottom is a member of one of the four other classes in the figure, aldehyde, ketone, ester, and alcohol.

methanol, only ethanol appears to have been identified in the ISM and comets (Zuckerman et al. 1975; Biver et al. 2015).

Acids—Figure 3 shows the two organic acids that were examined, formic and acetic, and both have been identified in the ISM (Zuckerman et al. 1971; Mehringer et al. 1997). The low vapor pressure of larger organic acids, and the possibility of permanent damage to our equipment, prevented an extension to a third compound. Perhaps these reasons explain why no comparable solid-phase n and ρ data for these organic acids were found in the literature.

Ethers—Two acyclic and two cyclic ethers were studied. Of these, only diethyl ether, $\text{O}(\text{C}_2\text{H}_5)_2$, seems not to be firmly identified in the ISM. See Snyder et al. (1974), Dickens et al. (1997), and McGuire et al. (2016) for more information. For dimethyl ether, $\text{O}(\text{CH}_3)_2$, we were unable to find, in either the refereed literature or standard reference works, peer-reviewed data on n and ρ , with these two properties measured at the same temperature. Accordingly, we used Braker & Mossman (1971) for $\rho(-25^\circ\text{C})$ and Francis (1960) for $n(25^\circ\text{C})$. For ethylene oxide, the only comparison data found were from measurements at 10°C (283 K), below the 20°C – 25°C range for most of the other compounds we examined.

Others—Figure 3's bottom row shows three other compounds for which we have measured and published a density and refractive index. They are included here for the sake of completeness.

See also Goesman et al. (2015) and McGuire (2018) for more on cometary and interstellar detections, respectively.

Table 2 gives n and ρ results for the thirty-two compounds of Figures 2 and 3, each studied as an amorphous ice at 15 K.

Compounds 1, 4, 8, 25, and 30 are from Hudson & Coleman (2019a), compounds 20, 23, and 31 are from Hudson & Coleman (2019b), and number 32, N_2O , is from Hudson et al. (2017). The remaining 23 sets of n and ρ values are new to this paper. Also in the table are values for the corresponding liquids, almost all studied at 20°C – 25°C .

4. Discussion

The results in Table 2 are available for immediate application to computing ice thicknesses, IR band strengths, optical constants, and abundances as relate to laboratory and extraterrestrial ices, which was our main goal. Other goals, as already stated, include the comparison of our ice results with liquid-phase data and particularly the examination of our data for trends in terms of molar refraction.

4.1. Ice and Liquid-phase Comparisons and Trends

The n and ρ values of Table 2 are compared to liquid-phase results in Figure 4. No obvious correlations are seen for the comparison of either n and ρ in parts (a) and (b) of the figure. Another type of comparison involves combining n and ρ values to get a molar refraction R_M using Equation (6). Table 3 gives R_M values and graph (c) of Figure 4 shows the comparison, with a striking degree of linearity between (i) the compounds we examined as amorphous ices and (ii) the corresponding liquid-phase compounds. As a first approximation, $R_M^{\text{liquid}} \approx R_M^{\text{ice}} + 0.3$ holds with a high correlation coefficient for the entire set of compounds studied, but individual chemical families deviated from this equation. Figure 5 shows plots of R_M for acyclic aldehydes,

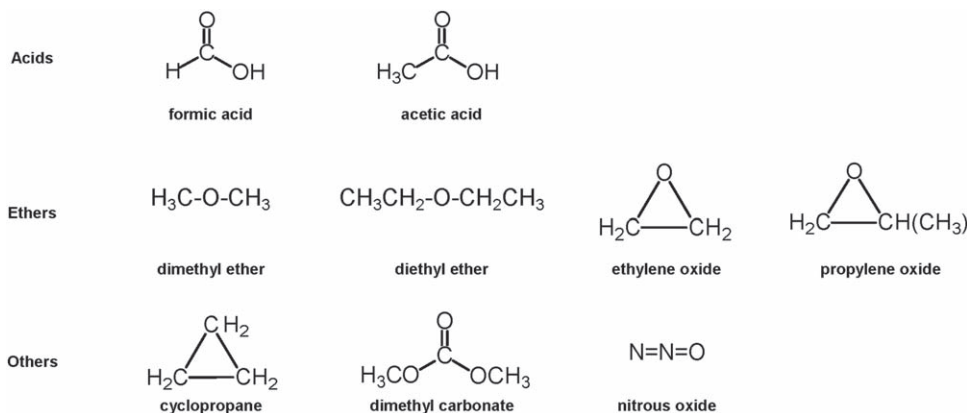


Figure 3. Simplified drawings of molecules examined in this work.

Table 2
Refractive Indices and Densities for Ices and Liquids^a

No.	Compound	Formula	n ice	ρ ice	n liquid	ρ liquid
1	acetaldehyde	HC(O)CH ₃	1.303	0.787	1.332	0.785
2	propionaldehyde	HC(O)CH ₂ CH ₃	1.326	0.778	1.362	0.805
3	butyraldehyde	HC(O)CH ₂ CH ₂ CH ₃	1.325	0.714	1.377	0.802
4	acetone	CH ₃ C(O)CH ₃	1.335	0.783	1.359	0.790
5	methylethyl ketone	CH ₃ C(O)C ₂ H ₅	1.319	0.721	1.379	0.805
6	3-pentanone	C ₂ H ₅ C(O)C ₂ H ₅	1.324	0.701	1.392	0.813
7	methyl formate	HC(O)OCH ₃	1.317	0.926	1.343	0.974
8	methyl acetate	CH ₃ C(O)OCH ₃	1.309	0.832	1.360	0.933
9	methyl propionate	CH ₃ CH ₂ C(O)OCH ₃	1.302	0.764	1.376	0.915
10	ethyl formate	HC(O)OCH ₂ CH ₃	1.276	0.784	1.359	0.921
11	ethyl acetate	CH ₃ C(O)OCH ₂ CH ₃	1.279	0.724	1.372	0.900
12	methanol	CH ₃ OH	1.296	0.779	1.329	0.791
13	ethanol	CH ₃ CH ₂ OH	1.319	0.739	1.360	0.789
14	1-propanol	CH ₃ CH ₂ CH ₂ OH	1.288	0.652	1.384	0.804
15	2-propanol	CH ₃ CH(OH)CH ₃	1.285	0.637	1.378	0.786
16	1-butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	1.308	0.651	1.399	0.810
17	2-butanol	CH ₃ CH ₂ CH(OH)CH ₃	1.298	0.638	1.397	0.808
18	allyl alcohol	H ₂ C=CH-CH ₂ OH	1.329	0.708	1.412	0.854
19	propargyl alcohol	HC≡C-CH ₂ OH	1.317	0.744	1.432	0.963
20	cyclopropane carboxaldehyde	<i>c</i> -C ₃ H ₅ -C(O)H	1.338	0.790	1.430	0.938
21	cyclopropane methyl ketone	<i>c</i> -C ₃ H ₅ -C(O)CH ₃	1.319	0.735	1.425	0.898
22	cyclopropane methyl ester	<i>c</i> -C ₃ H ₅ -C(O)OCH ₃	1.299	0.770	1.419	0.985
23	cyclopropane methanol	<i>c</i> -C ₃ H ₅ -CH ₂ OH	1.311	0.696	1.431	0.890
24	formic acid	HCOOH	1.291	0.979	1.371	1.220
25	acetic acid	CH ₃ COOH	1.300	0.892	1.372	1.049
26	dimethyl ether	O(CH ₃) ₂	1.309	0.801	1.300	0.724
27	diethyl ether	O(CH ₂ CH ₃) ₂	1.306	0.666	1.353	0.714
28	ethylene oxide	<i>c</i> -C ₂ H ₄ O	1.348	0.921	1.360	0.882
29	propylene oxide	<i>c</i> -C ₂ H ₃ O-CH ₃	1.324	0.775	1.367	0.859
30	dimethyl carbonate	(CH ₃) ₂ C(O)OCH ₃	1.295	0.903	1.369	1.069
31	cyclopropane	<i>c</i> -C ₃ H ₆	1.414	0.769	1.380	0.676
32	nitrous oxide	N ₂ O	1.317	1.263	1.338	1.255

Note.

^a Values for ices were measured at 15 K. Liquid values were measured near 20°C (ethylene oxide data is for 10°C) and are from standard compilations (e.g., Weast 1980). See Francis (1960) for approximate value of $n(\text{O}(\text{CH}_3)_2)$ and Braker & Mossman (1971) for the liquid's density. Data for liquid N₂O were obtained at 183 K (Living & Dewar 1892). For ices, n is for $\lambda = 670$ nm and for liquids $\lambda = 590$ nm. The units of ρ are g cm⁻³.

ketones, esters, and alcohols, molecular families for which we studied at least three members. The linearity of the data and a slope near 1 are obvious in each case, but the four y intercepts (offsets) are different. Figure 6 shows R_M values for the remaining compounds studied, encompassing cyclopropane, four cyclopropyl

derivatives, two acids, four ethers, a diester, and one inorganic compound (N₂O). Here too linearity is seen.

The top two panels of Figure 4 seem to suggest that there are no trends or patterns in our data for either n or ρ . However, Table 2 shows that the ice phase value of either property is

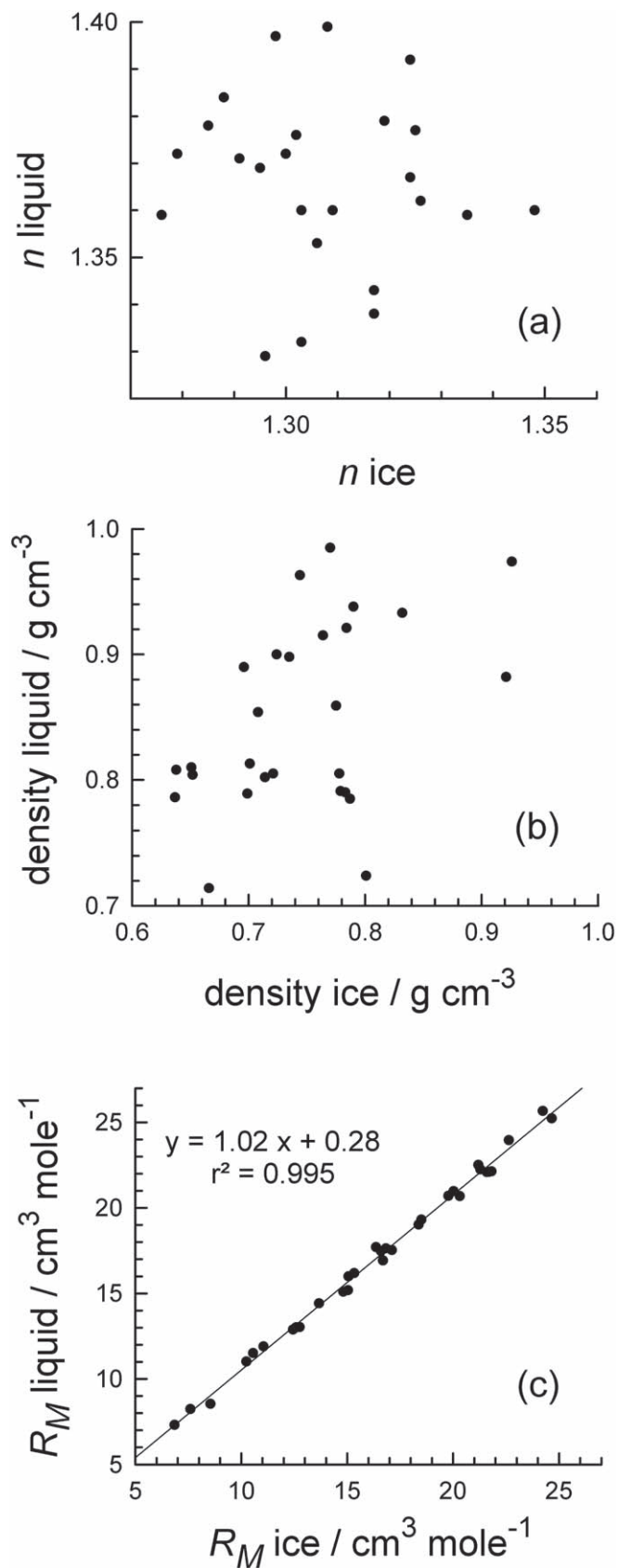


Figure 4. Data for amorphous ices at 15 K and liquids near room temperature. All values are taken from Tables 2 and 3.

almost always smaller than the liquid-phase value. A few exceptions can be found, and in almost every case involve a compound that is not a liquid in the 20°C–25°C range of all the other compounds examined (e.g., dimethyl ether). Another observation is that in a set of molecules differing by bonding along the series C–C, C=C, C≡C, the values of R_M for the first two compounds will be about the same, but larger than for the third member of the set. Our data show this trend with values of $R_M(1\text{-propanol}) \sim R_M(\text{allyl alcohol}) > R_M(\text{propargyl alcohol})$. For a literature example of this trend, see the liquid 3-carbon series propane, propene, and propyne (Grosse & Linn 1939). For the crystalline solids of Table 1, we found that each has a density larger than that of the corresponding amorphous ice, although temperature differences make rigorous comparisons difficult.

4.2. Measured and Calculated Molar Refractions

Molar refractions are approximately additive, which provides another way to test our results. In Figure 5's panel (a), moving from the lowest point to the middle point corresponds to the addition of one $-\text{CH}_2-$ group to the formula of the original molecule, acetaldehyde, to give propionaldehyde. Adding a second $-\text{CH}_2-$ group gives R_M for the top point in the panel, corresponding to butyraldehyde. In both cases, the increase in R_M for both liquids and ices is 4–5 $\text{cm}^3 \text{ mole}^{-1}$. The same pattern can be seen for the three points in panel (b) for ketones, and also is found on careful examination of the data in the other two panels of Figure 5, although more than three molecules are represented in each of those graphs.

Attempts going back to at least the mid-twentieth century, with roots stretching back to Newton (Kragh 2018), have been made to assign numerical values to atoms, groups of atoms, and chemical bonds in order to combine such values and arrive at R_M for any molecule. Although such work has focused on liquids, with little or no attention paid to the cryogenic solids of astrochemical relevance, it should be possible to verify additivity given a sufficiently large and varied number of measurements on ices. For our initial study with amorphous ices, we have adopted the method of bond contributions and the values of Denbigh (1940) to calculate R_M values. Bonds used (and contributions to R_M in $\text{cm}^3 \text{ mole}^{-1}$) were as follows: C–H (1.69), C–C (1.25), O–H (1.73), C–O (1.51), C=O (3.38), C=C (4.16), and C≡C (6.4). For example, from the five bonds of CH_3OH , one finds $R_M = 3(1.69) + 1.73 + 1.51 = 8.31 \text{ cm}^3 \text{ mole}^{-1}$. Figure 7 compares calculated R_M values for our compounds to our measured values for amorphous ices. The correlation between the observed and computed values is obvious. Admittedly, the agreement largely reflects the fact that the bond contributions used are from liquids, for which Figure 4(c) already shows reasonable agreement with our work, but nevertheless the linearity of Figure 7 for ices is gratifying.

4.3. Isomers and Molar Refractions

Isomeric pairs of molecules in which the number of each type of bond is the same provide another check on our results. For example, since the isomers propionaldehyde (propanal) and acetone each have six C–H bonds, two C–C bonds, and one C=O bond then on the basis of additivity the two compounds

Table 3
Molar Refractions of Ices and Liquids^a

No.	Compound	Formula	R_M ice ^b	R_M liquid ^b	R_M calculated ^c
1	acetaldehyde	HC(O)CH ₃	10.56	11.51	11.39
2	propionaldehyde	HC(O)CH ₂ CH ₃	15.06	16.00	16.02
3	butyraldehyde	HC(O)CH ₂ CH ₂ CH ₃	20.32	20.68	20.65
4	acetone	CH ₃ C(O)CH ₃	15.34	16.19	16.02
5	methylethyl ketone	CH ₃ C(O)C ₂ H ₅	19.78	20.70	20.65
6	3-pentanone	C ₂ H ₅ C(O)C ₂ H ₅	24.65	25.23	25.28
7	methyl formate	HC(O)OCH ₃	12.75	13.03	13.16
8	methyl acetate	CH ₃ C(O)OCH ₃	17.11	17.52	17.79
9	methyl propionate	CH ₃ CH ₂ C(O)OCH ₃	21.70	22.10	22.42
10	ethyl formate	HC(O)OCH ₂ CH ₃	16.36	17.71	17.38
11	ethyl acetate	CH ₃ C(O)OCH ₂ CH ₃	21.28	22.25	22.42
12	methanol	CH ₃ OH	7.60	8.24	8.31
13	ethanol	CH ₃ CH ₂ OH	12.44	12.89	12.94
14	1-propanol	CH ₃ CH ₂ CH ₂ OH	16.60	17.48	17.57
15	2-propanol	CH ₃ CH(OH)CH ₃	16.83	17.63	17.57
16	1-butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	21.81	22.15	22.20
17	2-butanol	CH ₃ CH ₂ CH(OH)CH ₃	21.59	22.09	22.20
18	allyl alcohol	H ₂ C=CH-CH ₂ OH	16.69	16.92	17.10
19	propargyl alcohol	HC≡C-CH ₂ OH	14.82	15.10	15.96
20	cyclopropane carboxaldehyde	c-C ₃ H ₅ -C(O)H	18.50	19.30	18.52
21	cyclopropane methyl ketone	c-C ₃ H ₅ -C(O)CH ₃	22.64	23.95	23.15
22	cyclopropane methyl ester	c-C ₃ H ₅ -C(O)OCH ₃	24.24	25.67	24.92
23	cyclopropane methanol	c-C ₃ H ₅ -CH ₂ OH	20.02	20.97	20.07
24	formic acid	HCOOH	8.55	8.55	8.31
25	acetic acid	CH ₃ COOH	12.59	13.01	12.94
26	dimethyl ether	O(CH ₃) ₂	11.06	11.90	13.16
27	diethyl ether	O(CH ₂ CH ₃) ₂	21.19	22.51	22.42
28	ethylene oxide	c-C ₂ H ₄ O	10.24	11.02	11.03
29	propylene oxide	c-C ₂ H ₃ O-CH ₃	15.04	15.18	15.66
30	dimethyl carbonate	(CH ₃ O)C(O)OCH ₃	18.37	19.02	19.56
31	cyclopropane	c-C ₃ H ₆	13.67	14.42	13.89
32	nitrous oxide	N ₂ O	6.85	7.31	...

Notes.^a The units of R_M are cm³ mole⁻¹.^b Values of R_M were calculated from the data of Table 2.^c Values of R_M were calculated from bond contributions. See the text.

should have about the same R_M value. Table 4 shows that for this pair of compounds and five others, the R_M values are within about 1 cm³ mole⁻¹ for our 15 K measurements on amorphous ices. A propagation-of-error analysis using Equation (6) leads to uncertainties in R_M of about 0.1 cm³ mole⁻¹ for the smaller molecules we studied up to about 0.4 cm³ mole⁻¹ for the larger ones. This implies that the values in Table 4 for isomers are within or almost within experimental error for our ices.

4.4. Comparisons to Earlier Work

The lack of published laboratory data corresponding to that in our Tables 2 and 3 makes it difficult to compare our results directly to those in the literature. To two decimal places, our n for amorphous methyl formate at 15 K is 1.32, near the 1.30 at 20 K reported by Modica & Palumbo (2010). Our n for amorphous CH₃OH at 15 K is 1.296, roughly the average of the 1.257 and 1.33 at 20 and 25 K, respectively, already published (Luna et al. 2018; Sciré et al. 2019). In an earlier paper we combined room-temperature data for methyl propionate and n for the corresponding amorphous ice to estimate ρ for amorphous methyl propionate at 16 K (Hudson & Mullikin 2019). The estimated density value was 0.702 g cm⁻³, in contrast to the measured value

of 0.764 g cm⁻³ reported here. The densities we determined for amorphous (15 K) and crystalline (120 K) CH₃OH are 0.778 and 1.02 g cm⁻³, respectively, compared to the 0.636 and 0.795 g cm⁻³ of Luna et al. (2018) at 20 and 120 K. As already stated, the density of crystalline CH₃OH from diffraction studies is 1.015 g cm⁻³ (Torrie et al. 2002).

4.5. Some Astrochemical Connections and Applications

The large number of n and ρ values presented here lead to several comments about the data and its use. To begin, all of the results in this paper are for single-component ices and not for the undoubtedly more-complex ice compositions of planetary surfaces and interstellar solids. However, data for individual ice components is critical for the accurate preparation of laboratory ice mixtures by vapor-phase deposition. The absolute concentrations (abundances) of ices in mixtures condensed onto a cold substrate can be determined by calibrations involving each component separately to determine its deposition rate, and for such calibrations our n and ρ values are needed.

Our Table 2 lists low-temperature results for ices alongside data for room-temperature liquids. In no case is the difference

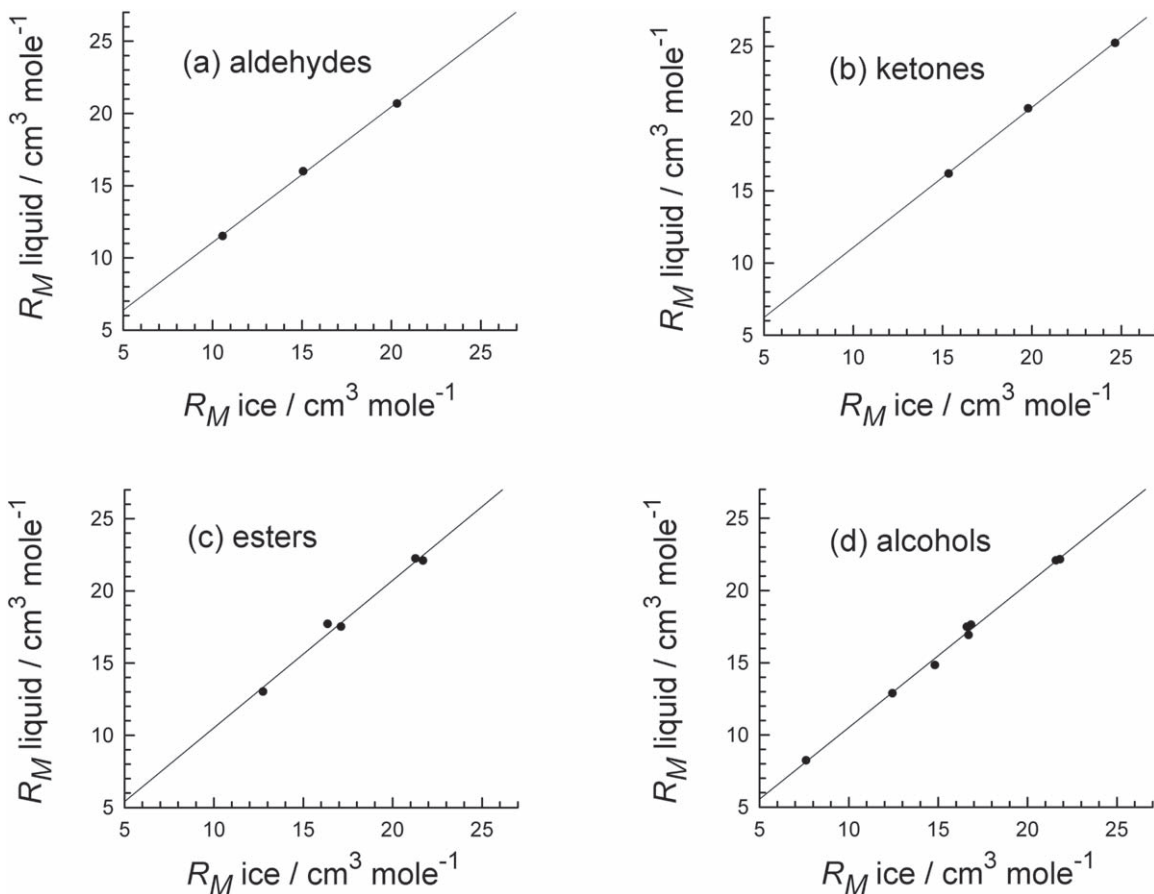


Figure 5. Molar refractions for amorphous (a) aldehydes, (b) ketones, (c) esters, and (b) alcohols at 15 K compared to values from liquids at 20°C–25°C. All values are taken from Table 3.

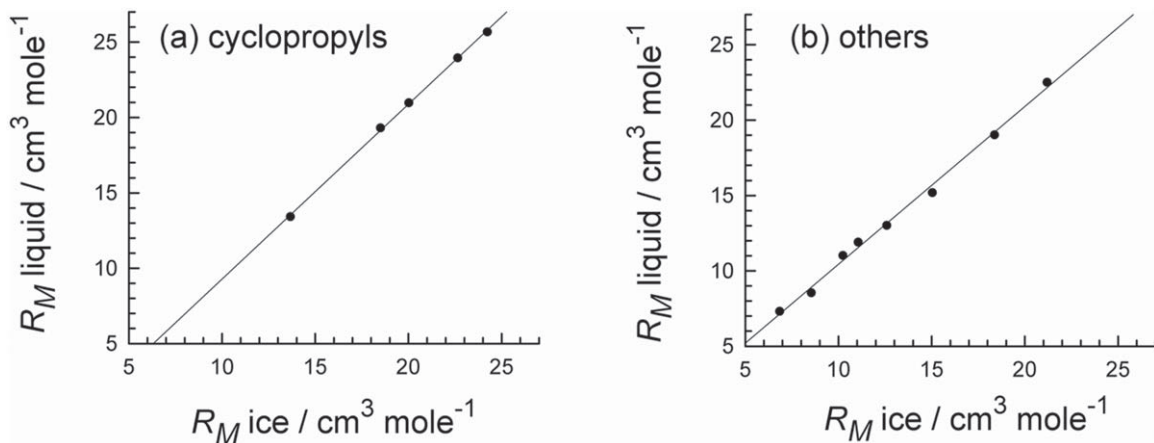


Figure 6. Data for amorphous (a) cyclopropane and four derivatives and (b) acids, ethers, dimethyl carbonate, and N_2O at 15 K compared to data from liquids near room temperature. See Table 3 for the data.

in n greater than 10%, so that simply adopting room-temperature n values to measure ice thicknesses with Equation (3) is unlikely to lead to larger uncertainties. However, the differences between ice densities and those of liquids can reach 20% in many cases, especially for the larger molecules, which can lead to errors in band strengths of that size when Equation (5) is used. We are unaware of any publication with this type of quantitative comparison between data for liquids and ices.

Our experience suggests that laboratory astrochemists are more likely to have the capability to measure ice thicknesses using n and interference fringes than to measure ρ , such as with a microbalance. In the absence of ice-density results, one option is to use Equation (6) or an equivalent form to calculate a density from a room-temperature R_M and an ice's n value. From Table 2, we estimate that the error in this approach is no more than about 10%, better than the possible 20% if a room-temperature ρ is used for an ice. See our work on ethanol

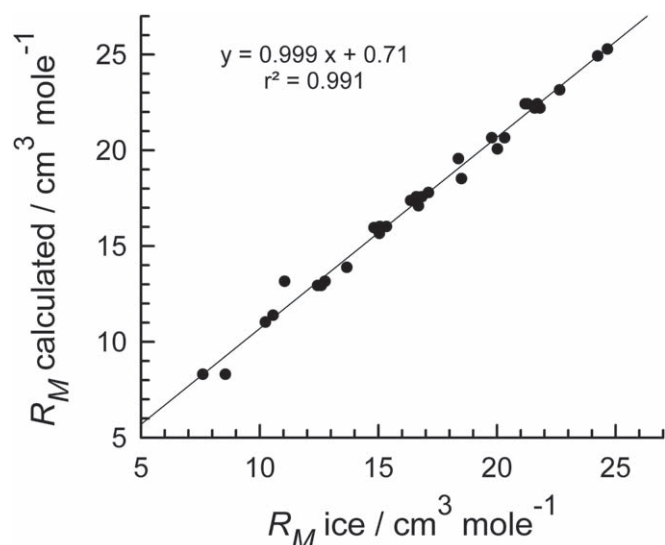


Figure 7. Molar refractions measured for amorphous ices compared to values computed with a bond-additivity approach. All values are taken from Table 3.

Table 4
Molar Refractions of Six Isomeric Pairs

No.	Compound	Formula	R_M Ice ^a
2	propionaldehyde	HC(O)CH ₂ CH ₃	15.06
4	acetone	CH ₃ C(O)CH ₃	15.34
3	butyraldehyde	HC(O)CH ₂ CH ₂ CH ₃	20.32
5	methylethyl ketone	CH ₃ C(O)C ₂ H ₅	19.78
8	methyl acetate	CH ₃ C(O)OCH ₃	17.11
10	ethyl formate	HC(O)OCH ₂ CH ₃	16.36
9	methyl propionate	CH ₃ CH ₂ C(O)OCH ₃	21.70
11	ethyl acetate	CH ₃ C(O)OCH ₂ CH ₃	21.28
3	1-propanol	CH ₃ CH ₂ CH ₂ OH	16.60
4	2-propanol	CH ₃ CH(OH)CH ₃	16.83
16	1-butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	21.81
17	2-butanol	CH ₃ CH ₂ CH(OH)CH ₃	21.58

Note.

^a The units of R_M are $\text{cm}^3 \text{mole}^{-1}$. Values of R_M are from Table 3.

(Hudson 2017), that of Modica & Palumbo (2010) on methyl formate, and the measurements of Romanescu et al. (2010) on a variety of compounds. We suggest that subsequent IR band strength measurements will be influenced by no more than this amount from such an approximation. Again, we are not aware of any previous study of the degree of error involved in combining data for liquids and ices to calculate an ice's density.

Our data and graphs show that molar refractions (R_M) of amorphous ices obey the expected trends of larger values with increasing molecular complexity, again adding confidence in our results. We also have found in the absence of laboratory data that bond contributions can be used to approximate R_M , so that if either n or ρ is known then the other can be calculated with reasonable confidence. Our Table 4 shows that the near-equality of R_M for isomers holds for amorphous ices. If an icy compound's R_M is needed but unavailable then the value for one of its isomers can serve as a reasonable substitute.

Concerning specific applications to astrochemical investigations in the literature, there are many investigations in which our results could have been useful either for measuring an ice

thickness or for deriving band strengths or optical constants for finding a molecular abundance. Examples include the study of Jonusas et al. (2017) involving 1-propanol and propionaldehyde, the work of Terwisscha van Scheltinga et al. (2018) on acetaldehyde, the examination of methyl acetate by Sivaraman et al. (2013), the very recent study by Bergner et al. (2019) with ethylene oxide, and the older investigation of acetic acid by Bennett et al. (2005). Lacking appropriate band strengths of acetaldehyde, which can be determined with our n and ρ , Fresneau et al. (2015) used results based on gas-phase measurements of formaldehyde cited by Schutte et al. (1993). The review of IR band strengths of astrochemically relevant molecules by Bouilloud et al. (2015) specifically mentioned that no measurements of either n or ρ were available for amorphous formic acid, which hinders any attempt at calculating its IR band strengths. For the present paper we have measured both n and ρ , and our values are listed in Table 2. See also our own study of ethanol for another example of how the lack of lab data necessitated the approximation of an ice's density, with little firm information on the degree of error involved (Hudson 2017).

Just as important as these applications and our numerical results is our demonstration that measurements on a series of ices need not be carried out with each compound treated in isolation. Consistency in measurements can and should be checked by the use of molecular structure considerations as well as trends in physical properties, such as temperature. We encourage continued checks of lab data for such consistency among astrochemically relevant molecules, such as of NH_3 results by a consideration of CH_3NH_2 and $\text{CH}_3\text{CH}_2\text{NH}_2$, comparisons of CO_2 measurements with results from OCS and CS_2 , and checks of measurements on formamide (HCONH_2) using data from methyl formamide ($\text{HCONH}(\text{CH}_3)$) and dimethyl formamide ($\text{HCON}(\text{CH}_3)_2$). No longer should each astrochemical measurement of n and ρ for an ice be considered an island of investigation, unrelated to results from other molecules.

5. Summary and Conclusions

A set of n and ρ values for amorphous ices has been measured with a single, uniform method and in a single experimental chamber. The results have been compared against room-temperature data for liquids to determine the degree of error in using the latter when ice data are unavailable. Values of molar refractions for the same ices have been calculated and compared against both liquid-phase R_M values and R_M values calculated from bond contributions. The expected trends have been verified for the first time for amorphous ices. Comparisons also have been made for R_M for isomers. The extent of error in using the Lorentz–Lorenz equation, specifically its modification to give molar refractions, is noted, and found to be relatively small for the organic compounds examined. The value of testing n , ρ , and R_M results using molecular structures as a guide has been demonstrated, emphasized, and encouraged.

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References

- Allamandola, L. J., Sandford, S. A., Tielens, A. G. G. M., & Herbst, T. M. 1992, *ApJ*, **399**, 134
- Allan, D. R., Clark, S. J., Ibberson, R. M., et al. 1999, *ChCom*, **8**, 751
- Ball, J. A., Gottlieb, C. A., Lilley, A. E., & Radford, H. E. 1970, *ApJL*, **162**, L203
- Belloche, A., Garrod, R. T., Müller, H. S. P., et al. 2009, *A&A*, **499**, 215
- Bennett, C. J., Osamura, Y., Lebar, M. D., & Kaiser, R. I. 2005, *ApJ*, **634**, 698
- Bergner, J. B., Öberg, K. I., & Rajappan, M. 2019, *ApJ*, **874**, 115
- Biver, N., Bockelée-Morvan, D., Moreno, R., et al. 2015, *SciA*, **1**, e1500863
- Bockelée-Morvan, D., Colom, P., Crovisier, J., Despois, D., & Paubert, G. 1991, *Natur*, **350**, 318
- Bouilloud, M., Fray, N., Bénilan, Y., et al. 2015, *MNRAS*, **451**, 2145
- Braker, W., & Mossman, A. L. 1971, *Matheson Gas Data Book* (5th ed.; Milwaukee, WI: Matheson)
- Brown, R. D., Crofts, J. G., Godfrey, P. D., et al. 1975, *ApJL*, **197**, L29
- Combes, F., Gerin, M., Wooten, A., et al. 1987, *A&A*, **180**, L13
- de Barros, A. L. F., da Silveira, E. F., Bergantini, A., Rothard, H., & Boduch, P. 2015, *ApJ*, **810**, 156
- de Smedt, J., & Keesom, W. H. 1924, *Proc. Koninklijke Akad. Van Wetenschappen te Amsterdam (Proc. Amsterdam Acad.)*, **27**, 839, Note that we have recalculated the density of N₂O using the most-recent value of Avogadro's constant
- Denbigh, K. G. 1940, *Trans. Farad. Soc.*, **36**, 936
- Dickens, J. E., Irvine, W. M., Ohishi, M., et al. 1997, *ApJ*, **489**, 753
- Fourikis, N., Sinclair, M. W., Robinson, B. J., Godfrey, P. D., & Brown, R. D. 1974, *AuJPh*, **27**, 425
- Francis, A. W. 1960, *J. Chem. & Eng. Data*, **5**, 534
- Fresneau, A., Danger, G., Rimola, A., et al. 2015, *MNRAS*, **451**, 1649
- Goesman, F., Rosenbauer, H., Bredelhöft, J. H., et al. 2015, *Sci*, **349**, aab0689
- Groner, P., Stolkin, I., & Günthard, H. H. 1973, *JPhE*, **6**, 122
- Grosse, A. V., & Linn, C. B. 1939, *JACS*, **61**, 751
- Heavens, O. S. 2011, *Optical Properties of Thin Solid Films* (2nd ed.; New York: Dover), 114, (Original printing: 1955, Butterworths Scientific Publ. London)
- Hollenberg, J., & Dows, D. A. 1961, *JChPh*, **34**, 1061
- Hollis, J. M., Jewell, P. R., Lovas, F. J., Remijan, A., & Møllendal, H. 2004, *ApJL*, **610**, L21
- Hudgins, D. M., Sandford, S. A., Allamandola, L. J., & Tielens, A. G. G. M. 1993, *ApJSS*, **86**, 713
- Hudson, R. L. 2017, *AcSpe*, **187**, 82
- Hudson, R. L., & Coleman, F. M. 2019a, *PCCP*, **21**, 11284
- Hudson, R. L., & Coleman, F. M. 2019b, *ECS*, **3**, 1182
- Hudson, R. L., Gerakines, P. A., & Ferrante, R. F. 2018, *AcSpe*, **193**, 33
- Hudson, R. L., Loeffler, M. J., & Gerakines, P. A. 2017, *JChPh*, **146**, 024304
- Hudson, R. L., & Mullikin, E. F. 2019, *AcSpe*, **207**, 216
- Jonusas, M., Guillemin, J.-C., & Krim, L. 2017, *MNRAS*, **468**, 4592
- Kragh, H. 2018, *Substantia*, **2**, 7
- Liveing, G., & Dewar, J. 1892, *PMag*, **34**, 205
- Loeffler, M. J., Moore, M. H., & Gerakines, P. A. 2016, *ApJ*, **827**, 1
- Lu, C. S., & Lewis, O. 1972, *JAP*, **43**, 4385
- Luna, R., Molpeceres, G., Ortigoso, J., et al. 2018, *A&A*, **617**, A116
- McGuire, B. A. 2018, *ApJS*, **239**, 17
- McGuire, B. A., Carroll, P. B., Loomis, R. A., et al. 2016, *Sci*, **352**, 1449
- Mehring, D. M., Snyder, L. E., Miao, Y., & Lovas, F. 1997, *ApJL*, **480**, L71
- Modica, P., & Palumbo, M. E. 2010, *A&A*, **519**, A22
- Nijveldt, D., & Vos, A. 1988, *Acta Cryst. B*, **44**, 281
- Öberg, K. I., Garrod, R. T., van Dishoeck, E. F., & Linnartz, H. 2009, *A&A*, **504**, 891
- Romanescu, C., Marschall, J., Kim, D., Khatiwada, A., & Kalogerakis, K. A. 2010, *Icar*, **205**, 695
- Satorre, M. Á., Domingo, M., Millan, C., et al. 2008, *PSS*, **56**, 1748
- Schutte, W., Allamandola, L. J., & Sandford, S. A. 1993, *Icar*, **104**, 118
- Sciré, C., Urso, R. G., Fulvio, D., Baratta, G. A., & Palumbo, M. E. 2019, *AcSpe*, **219**, 288
- Sivaraman, B., Nair, B. G., Lo, J.-I., et al. 2013, *ApJ*, **778**, 157
- Snyder, L. E., Buhl, D., Schwartz, P. R., et al. 1974, *ApJL*, **191**, L79
- Snyder, L. E., Lovas, F. J., Mehring, D. M., et al. 2002, *ApJ*, **578**, 245
- Tempelmeyer, K. E., & Mills, D. W. 1968, *JAP*, **39**, 2968
- Tercero, B., Kleiner, I., Cernicharo, J., et al. 2013, *ApJ*, **770**, L13
- Terwisscha van Scheltinga, J., Ligterink, N. F. W., Boogert, A. C. A., van Dishoeck, E. F., & Linnartz, H. 2018, *A&A*, **611**, A35
- Torrie, B. H., Binbrek, O. S., Strauss, M., & Swainson, I. P. 2002, *JSSCh*, **166**, 415
- Weast, R. C. 1980, *CRC Handbook of Chemistry and Physics* (61st ed.; Boca Raton, FL: CRC Press)
- Zuckerman, B., Ball, J. A., & Gottlieb, C. A. 1971, *ApJL*, **163**, L41
- Zuckerman, B., Turner, B. E., Johnson, D. R., et al. 1975, *ApJL*, **196**, L99