Monthly Notices
of the
ROYAL ASTRONOMICAL SOCIETY

MNRAS **485,** 861–871 (2019)
Advance Access publication 2019 February 6

doi:10.1093/mnras/stz254

Molecular identifications in experiments with astronomical ice analogues: new data, old strategies, and the N_2 + acetone system

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Accepted 2019 January 10. Received 2018 December 20; in original form 2018 December 20

ABSTRACT

A recent publication on the radiation chemistry and IR spectroscopy of N_2 + acetone ices is used to illustrate some of the difficulties encountered in the study of astronomical ice analogues. Concerns and problems are identified and suggestions for their solution are presented, including new infrared (IR) spectra of amorphous ices. The hazards of using peak positions alone for assignments of the IR spectra of irradiated ices are illustrated, and the importance of considering the underlying reaction chemistry is shown. Several experiments are proposed as a way to investigate the behaviour of acetone in cold, extraterrestrial environments. Electronic versions of IR spectra are provided and several new refractive indices of ices are reported.

Key words: astrochemistry – methods: laboratory – ISM: molecules.

1 INTRODUCTION

The study of infrared (IR) spectra of astronomical ice analogues has been underway for several decades in the US, Europe, Asia, and other locations. Among the problems investigated have been the spectral, chemical, and physical changes at various stages of alteration of ices by ionizing radiation. Radiation-induced decay rates have been measured, the trapping and release of gases has been examined, and reaction products have been identified, all with the goal of understanding low-temperature chemistry in environments as diverse as the interstellar medium (ISM), comets, and icy satellites.

Of the investigations just mentioned, molecular formation is among the more exciting as it carries the promise of predicting new astronomical discoveries and explaining those already made. However, there are formidable problems in the study of the IR spectra of ices that are not always appreciated, starting with the relatively low sensitivity of conventional IR methods and the fact that most IR spectra of ices consist of broad, overlapping bands that lack the specificity of high-resolution gas-phase IR data. Further, the quantification of IR spectra in terms of molecular abundances is not straightforward as intrinsic (absolute) band strengths are difficult to measure and often unavailable.

Among the goals of our own research group's work is the study of various molecules and ions at low temperatures in order to predict and understand results from astronomical observatories and spacecraft instruments. Because there are far more combinations of physical conditions and chemical agents to investigate than resources allow, it is necessary to seek trends in data and to compare results from various laboratories. For experiments involving the irradiation of astronomical ice analogues, the alternative can lead to interminable laboratory measurements in which ice temperature, composition, and phase are varied along with radiation dose, dose rate, energy, and identity (e.g. UV, X-ray, e^-, H^+), and chemical analyses involving a wide range of modern analytical techniques at both cryogenic and room temperatures.

In this paper we draw attention to a recent publication in this journal in order to illustrate some of the continuing challenges in the laboratory study of astronomical ice analogues with IR spectroscopy. Multiple problems are noted, some new results are presented, and suggestions are made to help reduce uncertainties.

2 BACKGROUND

2.1 The case of acetone – a recent publication

In studying the low-temperature radiation chemistry of acetone, we have encountered a recent paper by de Barros et al. (2018), which we will refer to as simply dB18 after the first author, on the ion irradiation of an N_2 + acetone ice at 11 K. Although we enthusiastically agree with the authors' goal of understanding organic chemistry in N_2-rich solar system and interstellar environments, that particular publication suffers from a substantial number of errors, uncertainties, and omissions concerning the assignment and quantification of infrared spectral bands. In that paper's second and third pages alone, several things caught our attention. Starting on page 2, the chemical formula for acetamide is incorrect. The flux of the authors' 40 MeV $^{58}Ni^{11+}$ beam is needed to reproduce and interpret the experiments described, but no beam flux was stated. The stopping power of the ice sample for the beam's 40 MeV $^{58}Ni^{11+}$ ions also is needed to evaluate the authors' results and to determine if the radiation doses used and the effects observed are astronomically relevant. However, no stopping power was given. The reference

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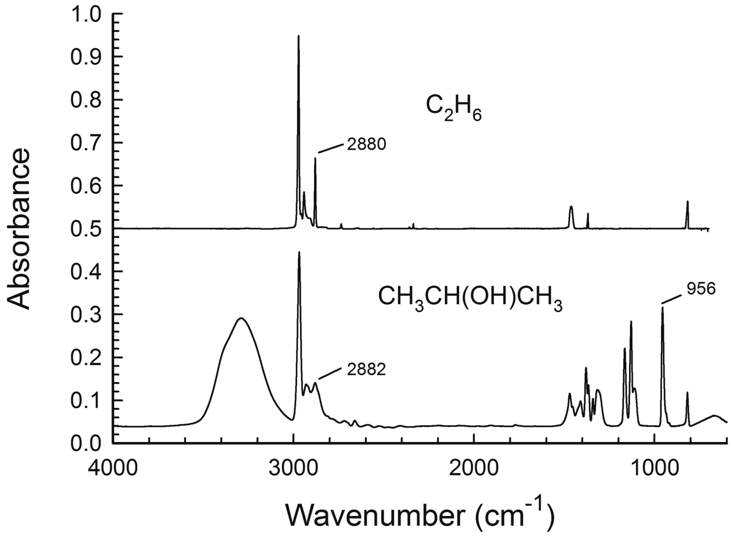

Figure 1. Infrared spectra of amorphous ethane (upper) and 2-propanol (lower), each ice made, and its spectrum recorded near 10 K. Spectra have been offset for clarity.

given for the IR band strength adopted for acetone (Andrade et al. 2014) is from an earlier density-functional calculation and was not checked against a laboratory measurement. This value (i) is used for calculations of acetone's column density before and after irradiations and (ii) enters into the extraction of cross-sections for various reaction products. Also on page 2, and continuing onto page 3, a band strength for N_2 was given and said to be calculated for a '10:1 N_2: CH_3COCH_3 mixture', but the method of calculation was not explained, and the paper cited does not cover acetone ices.

Turning from the text on pages 2 and 3 to the IR spectra shown there, we noted several unusual things in the figures, such as the following:

The four panels of Fig. 1 lack a vertical scale with numbers so that it is impossible to make quantitative comparisons with the paper's other IR spectra, such as those in Fig. 2.

The x and y axes in Fig. 1 are labelled differently than the x and y axes of Fig. 2, although presumably IR absorbance spectra are being shown in each case. The differences in the x-axis labels are perhaps trivial, but Fig. 2's y-axis label, 'Integrated Absorbance (a.u.)', is impossible for what is shown.

The ν_1 label in the top panel of Fig. 1 is above an IR feature near 2348 cm^{-1}, but that peak corresponds to the ν_3 asymmetric stretching vibration of CO_2. Presumably the ν_1 label was misplaced and actually pertains to the much smaller peak at 2328 cm^{-1} for N_2.

There are differences between the IR spectra of Figs 1 and 2 in the 2890 to 2790 cm^{-1} region. Fig. 1 shows what appears to be a featureless horizontal line between those limits, whereas Fig. 2 has an IR peak near 2827 cm^{-1}. It is not clear why the latter feature appears in Fig. 2, but not in Fig. 1.

Both Figs 1 and 2 show a well-resolved IR band near 1037 cm^{-1} that we have not seen in any published vibrational spectra of acetone other than one from the same authors' earlier work (Fig. 1; Andrade et al. 2014). Table 1 of dB18 assigns that IR band to acetone.

2.2 The case of acetone – a way forward

The aforementioned problems raise considerable doubts about the subsequent analysis, interpretation, and value of the authors' acetone results in terms of product yields, reaction cross-sections, and applications to extraterrestrial environments. The problems identified in that same paper cover IR spectral assignments, IR band strengths, reaction chemistry, and citations. Here we describe some of these problems and present new laboratory results to address them. New IR spectra of amorphous ices are shown to illustrate some uncertainties and remove some ambiguities.

3 EXPERIMENTAL SECTION

Much of the new results in this paper consist of a detailed analysis of an earlier publication. However, we also present new infrared spectra of amorphous icy solids along with several new refractive indices. As we will emphasize, the acquisition and application of reference spectra are invaluable for making and checking IR assignments of astronomical ice analogues.

For our laboratory work, chemical reagents were purchased from commercial suppliers, primarily Sigma Aldrich. Ice samples were prepared by vapour phase deposition and their IR spectra were recorded near 10 K with the same equipment and methods described in our recent publications (e.g. Gerakines & Hudson 2015a, 2015b; Hudson et al. 2018) or, in the cases of H_2CO and NH_3, similar equipment (Gerakines et al. 1996). The only compounds synthesized were H_2CO, HCN, and HNCO, following the procedures outlined in our earlier papers (Hudson & Moore 1995; Cottin et al. 2003; Gerakines et al. 2004). Note that IR spectra of H_2CO and NH_3 were taken from the work of Gerakines et al. (1996), which should be consulted for details. Ice temperatures varied from 9 to 16 K, but will be referred to simply as 10 K for convenience. The sole exception is the case of HCN, for which the amorphous ice was prepared and the spectrum recorded at 50 K.

Exact thicknesses of ice samples were not needed for the work presented here, but were measured as a check on day-to-day consistency. Ice thicknesses ranged from about 0.2 µm to about 3.2 µm. Thickness measurements were made for eight of our twelve ices using the method of interference fringes, in our case with a laser having $\lambda = 670$ nm (Hollenberg & Dows 1961; Groner et al. 1973; Hudson et al. 2017a). This method required us to know the index of refraction ($n_{\rm vis}$) of each ice at 670 nm, and in five cases $n_{\rm vis}$ had to be

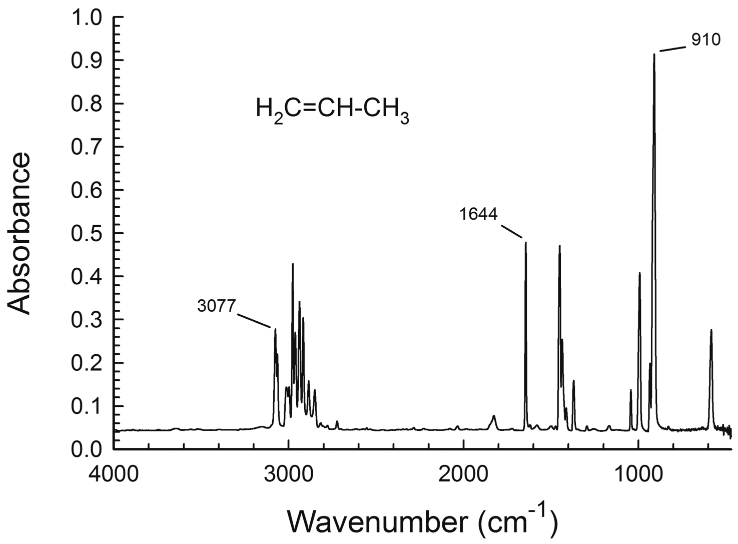

Figure 2. Infrared spectrum of amorphous propene (propylene). The ice was made and its spectrum recorded near 10 K.

Table 1. Selected data for molecular ices studied.

Compound	T (K)	n_{vis}[a]	Source
Ethane	13	1.34	Hudson et al. (2014)
2-Propanol	12	1.25	This work
Propene	9	1.38	This work
Acetic acid	13	1.29	This work
Methyl formate	16	1.30	This work
Methanol	10	1.26	Luna et al. (2018)
Ethanol	9	1.26	Hudson (2017)
1-Propanol	13	1.26	This work
Formaldehyde	10	[b]	Gerakines et al. (1996)
Ammonia	10	[b]	Gerakines et al. (1996)
HNCO	20	[c]	Lowenthal et al. (2002)
HCN	50	[d]	Moore et al. (2010)

Notes. [a] The wavelength we used to measure n_{vis} was 670 nm.

[b] The formaldehyde spectrum we show was for an ice with a thickness calculated by integrating the 1495 cm^{-1} band in Gerakines et al. (1996) and using *A*'(1495 cm^{-1}) from Bouilloud et al. (2015), the band strength being determined with $n_{vis} = 1.33$ and $\rho = 0.81$ g cm^{-3}. The ammonia spectrum we show was for an ice with a thickness calculated by integrating the 1070 cm^{-1} band in Gerakines et al. (1996) and using *A*'(1070 cm^{-1}) in Zanchet et al. (2013), the band strength being determined with $n_{vis} = 1.37$ and $\rho = 0.76$ g cm^{-3}.

[c] The HNCO thickness and n_{vis} for the spectrum we show are from Lowenthal et al. (2002). Note that the captions of that paper's Figs 1 and 2 are correct, but that the figures' IR spectra were mistakenly exchanged.

[d] The HCN thickness is based an absorption coefficient of $\alpha(2100\ cm^{-1}) = 17\,700\ cm^{-1}$ calculated from the optical constants in Moore et al. (2010), with those constants being dependent on a value of $n_{vis} = 1.30$.

measured as no reference data could be found. See Tempelmeyer & Mills (1968) for the two-laser method used. Our results are shown in Table 1 as averages of triplicate measurements, and all numbers are rounded to two decimal places. Uncertainties in n_{vis} for the five cases in Table 1 labelled 'This work' are no worse than ±0.01 and usually of the order of ±0.005. Additional measurements could reduce this uncertainty. For the compounds in Table 1's last four rows, thicknesses were estimated from either band areas or peak heights using reported IR band strengths or absorption coefficients.

Since our main concern was spectral assignments, it was relative band strengths, as opposed to absolute band intensities, that were of interest. Therefore, we emphasize that each IR spectrum in our figures was rescaled to fill the vertical space available.

4 RESULTS, OBSERVATIONS, AND ANALYSES

It is useful to begin this section by considering expectations for carbon-containing reaction products and IR spectral changes in an irradiated N_2 + acetone ice. From the molecular structure of acetone, two decompositions to molecular products are readily envisioned, each occurring by either a single elimination step or through multiple reactions. See (1) and (2) below.

$$CH_3C(=O)CH_3 \rightarrow CO + C_2H_6 \qquad (1)$$

$$CH_3C(=O)CH_3 \rightarrow H_2CCO + CH_4. \qquad (2)$$

Of the four products in these reactions, CH_4 will be the easiest to detect by solid-phase IR as this molecule has a strong absorbance near 1300 cm^{-1} clear of other strong IR bands. The CO and H_2CCO (ketene) molecules also have intense IR peaks, but aside perhaps from matrix-isolation experiments, the strongest IR absorptions of CO and H_2CCO in the solid state are nearly coincident, both being in the 2140–2120 cm^{-1} region (Hudson & Loeffler 2013 and references therein). The C_2H_6 (ethane) in the first reaction also will be hard to identify since its IR features tend to overlap with those of other compounds. For example, the reduction of acetone will give 2-propanol (isopropanol, $CH_3CH(OH)CH_3$), with many vibrational bands overlapping those of ethane (*vide infra*).

Beyond these reaction products, since nearly all irradiated solids forming CO also make CO_2, which has a strong, easily identified IR peak near 2340 cm^{-1}, one can predict that carbon dioxide will be identified in irradiated N_2 + acetone ices. One can also say that since nitrogen is present then OCN^- probably will form and be identified through a characteristic band near 2165 cm^{-1}, given the ease with which OCN^- is made in a variety of ices (Hudson et al. 2001). Other solid-state identifications of molecules and ions will be difficult as they are expected to be for products of small abundance and for weak overlapping features that lack the specificity of CO, CO_2, CH_4, and OCN$^-$. We also recognize that the ionizing radiation used in dB18 will amorphize any crystalline portions of the original sample and remove large portions of the matrix of non-polar molecules (i.e. N_2), resulting in a solid that is strongly organic in nature and somewhat more polar than the ice that began the experiment. For that reason, it is reasonable to use spectra of amorphous ices for product identifications.

Here we use table 3 of dB18 to illustrate some specific problems in the study of astronomical ices with IR spectroscopy and how such problems can be addressed. That table lists 18 reaction products from the irradiation of an N_2 + acetone ice at 11 K, all supposedly identified by IR spectroscopy, but there are concerns and questions related to each product in that same table. We discuss half of those products here, the remaining nine being covered in our appendix. Observations and comments labelled (a) refer mainly to chemistry and spectral assignments while those labelled (b) mainly concern IR band strengths. As it is important to give credit to researchers who make the measurements on which later work is based, and given the weight sometimes placed on journal impact factors and citation counts (bibliometrics), we also comment on various references in dB18.

4.1 Carbon monoxide, carbon dioxide, and methane

As already stated, it is safe to predict that CO will be a radiation product of acetone, but there is a concern with the spectral assignment in dB18 of an IR peak near 2140 cm^{-1} to CO. (i) Ketene (H_2CCO) also is an acetone decomposition product (e.g. Wilsmore 1907; Guenther & Walters 1959; Hudson 2018) and its strongest IR band overlaps that of CO, complicating any attempt to measure a CO reaction yield from IR spectra. This means that the CO abundances reported in dB18 may well be too large, increasing the uncertainty associated with that paper's CO cross-sections and elemental balances. The CO band in panel (b) of Fig. 2 in dB18 appears to show some asymmetry, which could be due to ketene formation, but the author's use of a dotted line to present the spectra degrades the apparent spectral resolution and hinders an independent evaluation. (ii) The CO band strength in dB18 is attributed incorrectly, the correct citation being to work in W. Person's laboratory (Jiang et al. 1975).

The assignment of an IR peak at 2348 cm^{-1} to CO_2 in dB18 almost certainly is correct, but again there are concerns. (i) The authors' unirradiated sample is contaminated with CO_2, which makes it is impossible, without additional information, to argue conclusively from the results published that CO_2 is a radiation product of acetone. Experiments with ^{13}C- or ^{18}O-labelled acetone would help to decide, as would control experiments in which the sample is allowed to sit unirradiated at 11 K or in which a blank substrate is ion-irradiated at 11 K. (ii) The CO_2 band strength is attributed incorrectly in table 3, the correct reference being to Yamada & Person (1964). It is assumed in dB18, but not stated, that the IR band strength of CO_2 in an amorphous N_2 + acetone mixture near 10 K is the same as in Person's crystalline CO_2 at 65–80 K.

The assignment of an IR peak near 1300 cm^{-1} to CH_4 (methane) in dB18 would appear to be firm since methane is not expected to be a contaminant, it is known to be a decomposition product of acetone, and it has a reasonably sharp IR peak in the 1300 cm^{-1} region, which is fairly uncluttered. (i) However, this CH_4 assignment could have been tested by using isotopically labelled acetone (e.g. acetone-d_6) or by slowly warming the irradiated sample to see if the 1300 cm^{-1} feature is lost before most others, as it should be given methane's volatility. (ii) The references cited for the CH_4 band strength adopted are two papers by some of the *MNRAS* paper's authors, but neither publication reported a new measurement of a CH_4 band strength (see Gerakines & Hudson 2015a for band strengths of amorphous CH_4).

4.2 Ethane and propene

Numerous organic products are expected from the irradiation of an acetone-containing ice, but identifying many of them in the solid state is difficult. (i) The suggestion that C_2H_6 (ethane) is a reaction product is reasonable, but the IR features assigned to ethane suffer from severe overlap with bands of other molecules. For example, the spectra in our Fig. 1, recorded in our laboratory, show that 2-propanol, a known product of acetone radiolysis (e.g. Barker 1962; Kučera 1965; Akhtar et al. 1975), has IR peaks in some of the same regions as C_2H_6, including for the feature near 2880 cm^{-1} used in dB18 to follow ethane formation. This overlap makes an assignment to just one compound difficult. Because of this ambiguity, the ethane assignment has to be rejected. (ii) The C_2H_6 band strength adopted by dB18 is an old value. One of the references is again to previous work by some of the authors, but the paper cited does not include a band-strength measurement (see Hudson et al. 2014a or Molpeceres et al. 2016 for measurements of band strengths and optical constants of amorphous ethane).

Propene (propylene, C_3H_6) is not expected to be a major decomposition product of acetone, and it is not clear how an IR-detectable quantity of propene could be made in an N_2 + acetone ice. (i) Of the five peaks listed for C_3H_6 in table 3 of dB18, two overlap with, and may be from, residual acetone (1438, 1420 cm^{-1}), another disagrees with the peak position labelled for propene in the authors' Fig. 3(c) (937 cm^{-1}), and a fourth peak (1174 cm^{-1}), also in Fig. 3(c), overlaps with a feature labelled for acetic acid, and it is not seen in our own reference spectra. The fifth and final C_3H_6 peak listed, at 3092 cm^{-1}, was used to quantify propene's abundance, but again that peak does not appear in IR spectra recorded in our laboratory (see our Fig. 2). Note that our spectrum shows that if a propene peak is present near 3092 cm^{-1} then several much stronger peaks also should be present, such as near 1644 and 910 cm^{-1}, but no such features appear in the spectra of irradiated N_2 + acetone in dB18. (ii) The citation given for the band strength used for C_3H_6 appears to be a NIST web page on mass spectra, but just how the IR band strength was determined from mass spectral data is not explained. In the absence of an appropriate reference spectrum and more details, the propene assignment cannot be accepted.

4.3 Acetic acid

The four IR peaks listed for acetic acid (CH_3COOH) in table 3 of dB18, at 2244, 1181, 1166, and 847 cm^{-1} are not close to any strong peaks in our acetic acid spectrum shown in Fig. 3. For example, the two peaks listed by dB18 near 1170 cm^{-1} have a separation of 15 cm^{-1}, but that region is essentially featureless in the IR spectrum of acetic acid. (i) The authors again cite a paper from their own work, but the four peaks of interest are not in it. Lacking a reference spectrum, the acetic acid assignment cannot be accepted. (ii) Again a citation is given to work by some of the authors to support the band strength adopted, but the cited paper does not describe a band strength measurement for acetic acid. Instead, it concerns work by Modica & Palumbo (2010) on methyl formate, a different molecule. In short, the IR band strength adopted for acetic acid is actually for

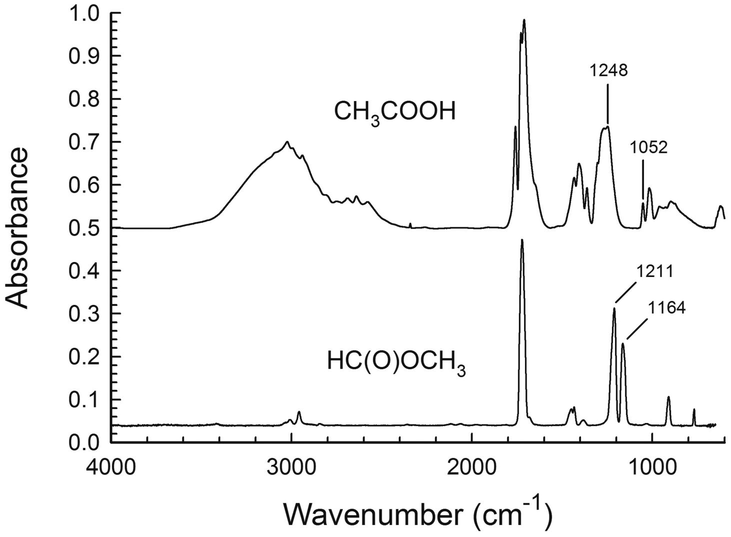

Figure 3. Infrared spectra of amorphous acetic acid (upper) and methyl formate (lower), each ice made and its spectrum recorded near 10 K. Spectra have been offset for clarity.

methyl formate, a different compound. We also note that the four peaks listed for acetic acid by dB18 do not match the spectrum of methyl formate seen in our Fig. 3 for comparison.

4.4 O_2 and N_3

It is hard to see how sufficient O_2 could be formed in the radiolysis of solid N_2 + acetone in dB18 to produce the weak IR-forbidden band of O_2 near 1550 cm^{-1} (St. Louis & Crawford 1962) unless the authors' sample was contaminated by atmospheric oxygen. Two IR positions were given for O_2 and once more the reference was to work by some of the same authors. That publication, in turn, gives the original source of the 2139 cm^{-1} peak as Vandenbussche et al. (1999), but that particular paper has been misread. The 2139 cm^{-1} peak listed in it is for CO, not for O_2.

It would be surprising if the N_3 free radical was not produced in the irradiation of N_2 + acetone, but no N_3 peak was shown and labelled as such by dB18. The arrow for N_3 in their Fig. 2(c) does not originate at a peak in the spectrum, but rather from or nearly from the side of a ^{13}C feature in the IR spectrum of unirradiated N_2 + acetone ice. (i) Three peak positions are listed for N_3 in dB18's table 3, but the reference cited gives only one peak (Jamieson et al. 2005). Our own literature search found a later paper from the same laboratory (Jamieson & Kaiser 2007) that gives a second N_3 peak (1657 cm^{-1}). The third peak listed by dB18 is at 1160 cm^{-1}, but Wu et al. (2012) assigned it to N_3^+, not N_3, based on an even earlier publication by Dyke et al. (1982). In short, a third misreading of the literature has occurred. Without better supporting evidence it is difficult to accept the N_3 assignment in dB18. (ii) The authors' choice for an N_3 band strength of 2.3×10^{-18} cm molec^{-1} is not found in the paper cited, which gives a value of 4.0×10^{-17} cm molec^{-1} instead. A third value, 2.3×10^{-19} cm molec^{-1}, from a previous paper by some of the authors (de Barros et al. 2015), disagrees with both of the numbers just given. The latter value is based on spectra with multiple N_3 features, but with relative intensities that contradict earlier work (e.g. Tian et al. 1988). Suffice it to say that there is an inconsistency in the N_3 citation given in dB18 and that a large uncertainty in the band strength of N_3 exists.

4.5 OCN and OCN^-

As with CH_3COOH, O_2, and N_3, a misreading of the literature plagues the 'OCN' work in dB18. In their text, the authors refer to 'Two isocyanto radical bands' with peaks at 2165 and 1948 cm^{-1}, both also being listed in that paper's table 3. However it is doubtful that either peak is for the OCN free radical as the published position of OCN in N_2 is not the authors' 1948 cm^{-1}, but rather ~1935 cm^{-1} (Milligan & Jacox 1967). We suggest that the peak at 1948 cm^{-1} is more likely from allene, $H_2C = C = CH_2$, based on earlier work with irradiated acetone that included isotopic substitution, among other aids (Hudson 2018 and references therein). We also suggest that the IR band at 2165 cm^{-1} in dB18 is due to OCN^-, the cyanate anion, based on that band's position, width, and the near ubiquity with which it is produced in a variety of irradiated solids made of O-, H-, C-, and N-containing molecules (Hudson et al. 2001). It is possible to distinguish OCN from OCN^- by thermal annealing as the anion is relatively stable at room temperature, but the radical is not, yet no such warming was reported. Note also that the OCN band strength used in dB15, from Sicilia et al. (2012), appears to be a value assumed by the latter authors in the absence of a measured value. Direct measurements of an infrared band strength for OCN in solids, as with the isoelectronic N_3 radical, seem not to have been reported. Additional work is needed to test our anion assignment and to quantify the abundance of OCN^-. Isotopically labelled reagents would be useful for distinguishing between OCN and OCN^-.

4.6 Other reported products

The remaining nine radiation products listed in table 3 of dB18 are treated in our appendix. For these products, there are questions about the clarity of the spectral features, the uniqueness of the assignments, the calculated abundances, and the strength and accuracy of the supporting references. For example, band strengths for three nitrogen oxides in the solid phase are needed, but calculated values from the gas phase are adopted without either explanation, the original reference, or laboratory comparisons to the calculated positions (see our appendix for details).

4.7 Some comments and conclusions

From the preceding sections we conclude that of the 18 N_2 + acetone reaction products tabulated by dB18, the CH_4 assignment probably is the most secure. The CO assignment also probably is correct given what is known of acetone's decomposition chemistry, but it needs checking to determine if ketene also is present and corrupting the CO band's integration. Similarly, the CO_2 assignment probably is correct, but work is needed to determine if atmospheric contaminants also contribute to the CO_2 band's area. The most promising ion assignment is OCN^-, as already discussed. Unfortunately, all of the remaining IR assignments have problems, some more severe than others, and so must be rejected until new experiments are reported to test them. The implication of all this is that the cross-sections, reactions yields, and 'atom budget' results published in dB18 also are suspect and require more work.

5 DISCUSSION AND SUGGESTIONS

5.1 Infrared spectral assignments and band strengths

Many of the problems and concerns identified here for N_2 + acetone ices apply to laboratory work on other astronomical ice analogues too. There are several strategies for addressing or avoiding such problems, and four such strategies quickly come to mind:

First, experiments with low-temperature ices can suffer from leaks in vacuum systems. One can test for such leaks by irradiating a blank substrate to see if products, such as CO, N_2O, and O_3, form from cryo-deposited atmospheric CO_2, N_2, and O_2. Another control experiment involves simply cooling an ice sample and waiting to see if contaminants deposit on it.

Second, most laboratory systems for measuring IR spectra of ices are capable of varying a sample's temperature. Warming an ice in which reactions have been initiated, as by radiolysis in the present case, allows one to correlate band intensities with temperature and to test IR assignments. Free radicals and small molecules with little or no dipole moment typically are the first influenced by temperature increases.

Third, isotopic substitution has long been used to test spectral assignments. In the case of the N_2 + acetone work in dB18, one or more isotopic shifts are known for essentially all of the products reported by the authors. Radiation experiments with $^{15}N_2$ + acetone would show isotopic shifts for nitrogen-containing product molecules.

Fourth, IR assignments to specific molecules and ions should always be tested by comparison to reference spectra of those same species. Ideally, such reference measurements are made with the same equipment used for one's own experiments, but several electronic collections of IR spectra of molecular ices are now available, although there is still relatively little sharing of such laboratory data (see Table 2 for six sources of IR spectra and one under construction). It must be emphasized that IR assignments based only on literature peak positions, much less a single peak's position, and without considering intensities and the underlying chemistry are of limited value for any but the simplest ices.

Some of these strategies may seem obvious, but for the acetone work in dB18 no mention was made of blanks, warming was said not to have been carried out, no experiments to test IR assignments by measuring isotopic shifts were reported, and no reference spectra were shown alongside the authors' results, which would have been especially helpful for assignments of weak IR features. None of these suggestions and strategies are especially new, but since laboratory astrochemistry is a multidisciplinary field perhaps they bear repeating periodically.

Concerning IR band strengths, as stated in our Introduction, intrinsic (absolute) band intensities of ices can be difficult to measure. Often one must be content with a band strength measured at a different temperature than that desired or from an ice sample with a somewhat different composition. As of this writing, neither computed band strengths, such as from density functional methods, nor gas phase IR intensities have been shown to be an adequate substitute for solid phase reference measurements. This is important to recognize since inaccurate or inappropriate band strengths can carry over into large uncertainties in, for example, rate constants and reaction yields.

5.2 Radiation chemistry and radiation sources

The paper of dB18 is an ambitious attempt at a quantitative study of the radiation chemistry of an N_2 + acetone (10:1) ice. As such, it would have been strengthened by a tighter connection to molecular-level chemistry and the photo- and radiation-chemical literature. Specific reactions were not shown and used in dB18 to predict and interpret the spectroscopic changes observed, and the spectral assignments seem not to have been aided with previous radiolytic work on acetone in other laboratories.

The formation of products in irradiated acetone has recently been reviewed, so it is not necessary to repeat here the various reactions studied (Hudson 2018). The obvious difference between radiolyses of neat acetone and an N_2 + acetone (10:1) mixture is that in the latter case N_2 molecules will absorb the majority of the energy delivered by the incident radiation. Bond breakage to make N atoms can be expected, and evidence for these can be obtained by warming the irradiated ice and observing the glow of the resulting nitrogen-atom emission (Peyron & Broida 1959; Tian & Michl 1988). Ionization of N_2 will form the radical cation $N_2{}^+$, and since acetone has a lower ionization energy than N_2, a charge transfer will occur as follows:

$$N_2{}^+ + (CH_3)_2CO \rightarrow N_2 + (CH_3)_2CO^{+\bullet} \qquad (3)$$

This reaction produces the acetone radical cation, the same species formed in the absence of N_2 (e.g. Belevsky et al. 1986). As the N_2 in the ice is depleted (vide infra) on continued irradiation, the dominant chemistry will increasingly resemble that of neat acetone. Again, see Hudson (2018) and references therein.

As for radiation sources, we have used the SRIM software to calculate that the electronic stopping power (S_{el}) of N_2 for the 40 MeV $^{58}Ni^{11+}$ ions used in dB18 is of the order of 3000–3500 keV μm^{-1}, depending on the precise density, composition, and compound corrections assumed (Ziegler 2013). With an ion beam of such a large stopping power, all analyses of chemical change in an N_2-rich ice are complicated by sample loss through sputtering of both reactants and products. It is therefore not surprising that fig. 5 of dB18 shows that the irradiation of an N_2 + acetone ice at 11 K destroyed or removed well over 99 per cent of the ice's N_2 molecules. Put differently, the chemistry occurring with the first irradiation, with the ice dominated by N_2, is substantially different from that at the final irradiation, at which point the great majority of the N_2 initially present has been lost. In contrast, we find from a similar SRIM calculation that S_{el} is only ~20 keV μm^{-1} for 1 MeV H^+ incident on solid N_2. A separate report suggests a value on the order of 6 keV μm^{-1} for 5 keV electrons (Jamieson et al. 2005). Such smaller stopping powers, compared to 3000–3500 keV μm^{-1}

Table 2. Selected data bases of mid-infrared spectra of molecular ices.

Host	Address
NASA Goddard Space Flight Center, USA	https://science.gsfc.nasa.gov/691/cosmicice/
NASA Ames Research Center, USA	http://astrochemistry.org/databases.php
Sackler Laboratory, Leiden University, The Netherlands	http://icedb.strw.leidenuniv.nl/
Universidade do Vale do Paraíba, Brazil	https://www1.univap.br/gaa/nkabs-database/data.htm
Catania Astrophysical Observatory, Italy	http://www.oact.inaf.it/weboac/labsp/
Grenoble Astrophysics and Planetology Solid Spectroscopy and Thermodynamics, France	https://ghosst.osug.fr/
OSUG data center/Université Grenoble Alpes, France	https://www.sshade.eu/ (under construction)

for the 40 MeV $^{58}Ni^{11+}$ ions used in dB18, significantly lessen the complications from sputtering and bulk, near-catastrophic changes in composition. Whatever case might be made for irradiating ices with heavy, highly-charged ions of low-abundance in cosmic rays has to be balanced against the subsequent difficulty in unraveling the extensive chemical and physical complications that they produce compared to the use of electrons and the more-abundant, lower-mass cosmic-ray ions.

5.3 Astrochemical connections

Having carried out a detailed analysis of a set of low-temperature N_2 + acetone radiation chemical experiments, it is appropriate to consider connections to astronomical problems. Acetone has been identified in interstellar and solar system environments, but in all cases either by remote sensing or in-situ sampling in the gas phase (e.g. Combes et al. 1987; Goesmann et al. 2015) as opposed to the solid state. However, given acetone's complexity (i.e. 10 atoms, 3 elements) it seems reasonable to postulate this molecule's formation and evolution in icy solids as opposed to the gas phase. For its synthesis we can point to recent work to make propylene oxide through the irradiation of CO_2 + propylene ices, both being known interstellar compounds (Hudson et al. 2017b). Isomerization of the latter is expected to give acetone and propanal. Therefore, it is not surprising that propylene oxide, acetone, and propanal all are known to be interstellar.

Just as important as acetone's formation are its subsequent chemical reactions to make other complex molecules. These have been studied by many workers and the resulting products identified for a variety of conditions. Certainly the isomerization

$$(CH_3)_2CO \rightarrow HC\,(O)\,CH_2CH_3 \tag{4}$$

to make propanal is one type of reaction expected, and its occurrence will complicate all infrared work of the type covered in this paper. Propanal can be reduced to 1-propanol (*n*-propyl alcohol), another complication to solid-phase IR identifications. See Jonusas et al. (2017) for a recent study involving this alcohol.

A different acetone isomerization will give 1-propene-2-ol, a vinyl alcohol

$$(CH_3)_2CO \rightarrow H_2C = C\,(OH)\,CH_3 \tag{5}$$

that will clutter the 1600 cm^{-1} infrared region with a C = C stretching vibration and the 1500–1000 cm^{-1} region with a variety of skeletal modes (Zhang et al. 1997). Such alcohols, properly called enols, are unstable relative to their aldehyde and ketone isomers, but would make good candidates for interstellar searches (Wang et al. 2008).

A third type of acetone reaction recognizes that NH_3 (ammonia) is a well-known component of interstellar and solar-system ices. Therefore, radiolysis or UV photolysis of the NH_3 + acetone combination might give an amination reaction such as

$$NH_3 + (CH_3)_2CO \rightarrow (CH_3)_2C\,(OH)\,NH_2 \tag{6}$$

to make an amino alcohol. Again, this reaction could cause considerable spectral confusion in the laboratory IR spectra of interstellar ice analogs, but it might lead to a gas-phase molecule and discovery.

As for new experiments, it would be useful to carry out N_2 + acetone irradiations with 1 MeV H^+, keV electrons, or far-UV photons to search for reaction products and reduce complications from ion-induced sputtering. It also would be useful to irradiate argon + acetone ices both to simplify the IR spectra by eliminating nitrogen-containing products and to reduce the uncertainty about their source.

5.4 Final comments

We close by emphasizing several points made earlier:

(i) Familiarity with the relevant spectroscopic and radiation-chemical literature and an understanding of the underlying reaction chemistry are crucial for assigning IR bands in irradiated or photolyzed ices.

(ii) It is difficult to make convincing and unique single-peak IR assignments in irradiated ices based solely on peak positions taken from the literature, as opposed to basing assignments on multiple IR bands and band intensities in conjunction with isotopic shifts and thermal behavior.

(iii) Before embarking on a program to generate large amounts of quantitative data, graphs, and tables, in irradiated or photolyzed ices it is important to possess reliable reference data, both IR spectra and band strengths. Along these lines, electronic copies of the spectra in the six figures of this paper are being posted on our research group's website.[1]

(iv) We stress the difficulty of using conventional IR spectroscopy to make firm assignments of reaction products in icy solids. Our own experience is that organic molecules with about ten atoms, such as propylene oxide and acetone, are near the method's limit (Hudson et al. 2017b; Hudson 2018). Even before that limit, multiple approaches, such as those just listed, are required. However, beyond about ten atoms the advantages of the IR approach for *in situ* product identification and quantification give way to other methods in which product molecules, particularly those of trace abundance, must be removed from the ice for identification (e.g. Henderson & Gudipati 2015; Abplanalp & Kaiser 2017).

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[1] https://science.gsfc.nasa.gov/691/cosmicice/

As always, it is incumbent on those reporting new results to support and justify them. We trust that the analysis and spectra presented here will help others, and the present authors, to do so.

ACKNOWLEDGEMENTS

This work was supported by the NASA Astrobiology Institute through funding awarded to the Goddard Center for Astrobiology under proposal 13-13NAI7-0032. Support also is acknowledged 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.

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APPENDIX

Nine of the 18 radiation products listed in table 3 of dB18 have been addressed in our Section 4. The remaining nine are examined here.

CH_3OH – It is difficult to see how CH_3OH (methanol) could readily form in an IR-detectable abundance in irradiated anhydrous N_2 + acetone, and we are unaware of claims in the radiation-chemical literature on acetone for this product (e.g. Barker 1962; Kučera 1965; Akhtar et al. 1975). (i) One of the stronger features ($\sim$1027 cm^{-1}) assigned to CH_3OH in dB18 is near a large peak in the unirradiated N_2 + acetone ice that was not seen by others working with acetone, raising the possibility of a small methanol contamination in the original sample. A reference spectrum of CH_3OH, seen in our Fig. A1, shows that its IR peak at 1460 cm^{-1}, used in dB18 to quantify methanol's abundance is considerably smaller than the peak near 1027 cm^{-1} different from what is seen in the Fig. 2(d) of dB18. Our Fig. A1 also shows that both ethanol and 1-propanol also absorb in the 1460 cm^{-1} region, and so the methanol spectral assignment cannot be taken as unique.

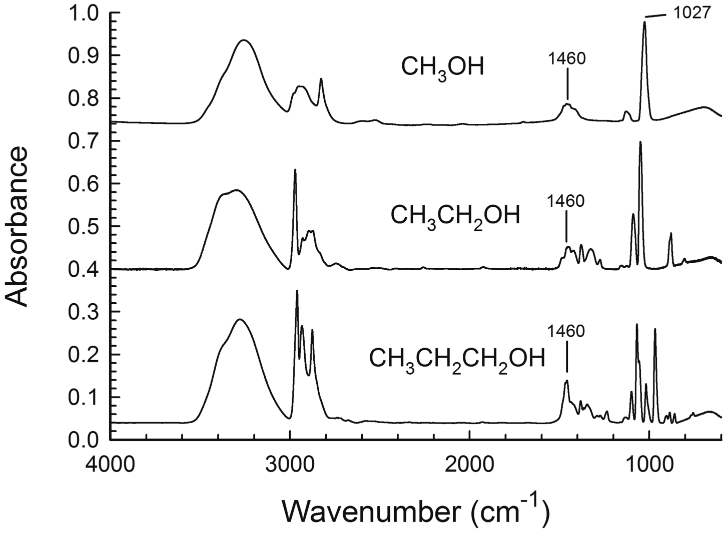

Figure A1. Infrared spectra of amorphous methanol (upper), ethanol (middle), and 1-propanol (lower), each ice made and its spectrum recorded near 10 K. Spectra have been offset for clarity.

(ii) The reference given for a methanol IR band strength is to the authors' own work, but it appears to originate in a measurement by Palumbo et al. (1999). The CH_3OH peak used for abundance calculations sits on the side of a much larger feature seen after irradiation, and it is not clearly stated how the two were separated for accurate integration. Note that mid-IR spectroscopy has been used by many research groups to study the chemistry of solid CH_3OH (e.g. Allamandola et al. 1988; Moore et al. 1996; Palumbo et al. 1999; Bennett et al. 2007; Saenko & Feldman 2016; Sullivan et al. 2016).

H_2CO – Since CO is a radiation product of acetone then H_2CO (formaldehyde) might be made by H-atom addition to CO, among other paths. (i) However, the features assigned to H_2CO by dB18 are not convincing. The authors assign a peak at 1758 cm^{-1} to H_2CO, but that position is substantially different from the 1740 cm^{-1} for an $N_2 + H_2CO$ ice in the reference cited (Bohn et al. 1994) and from the values of Schutte et al. (1993) of 1723 cm^{-1} for neat H_2CO and 1719 cm^{-1} for H_2CO in H_2O ice. Also, the 1758 cm^{-1} peak of dB18 is nearly coincident with a combination band in the spectrum of unirradiated acetone (Harris & Levin 1972), raising a question about how the alleged H_2CO feature was extracted and integrated (see also our Fig. A2 for a formaldehyde spectrum). Given these concerns, the one-peak H_2CO assignment cannot be accepted without more work. (ii) A band strength for H_2CO was adopted, but the references cited did not describe as to how it was measured. One of those references cites Schutte et al. (1993) who gave a band strength based on a comparison to an $H_2O + H_2CO$ mixture and an assumption of equality for the carbonyl stretching band's intensity in the two ices.

NH_3 – Concerns also surround this assignment. (i) What is labelled as NH_3 (ammonia) in Fig. 2(c) of dB18 is only a sloping feature and not a peak. A feature near 1070 cm^{-1} in Fig. 2(d) is labelled NH_3, but it is weak and traced with a broken line that reduces its shape to a single point. It also overlaps with a ^{13}C peak for acetone in the original unirradiated ice, raising doubts about it being from a radiation product. Table 3 also lists an ammonia peak at 950 cm^{-1}, but neither the NH_3 spectrum of our Fig. A2 nor spectra of others (e.g. Zheng & Kaiser 2007) show such a feature for NH_3, although there is one near there for 2-propanol. Note also that 1-propanol has a peak near 1070 cm^{-1}. Given all of this, it is difficult to accept the authors' NH_3 assignment as definitive without stronger IR evidence, such as a reference spectrum for NH_3 placed alongside the authors' spectra and a consideration of alternative assignments that excludes them. (ii) The NH_3 band-strength reference given in the authors' table 3 is incorrect. The value used originated in d'Hendecourt & Allamandola (1986). Results from better and more-recent measurements are available (e.g. Zanchet et al. 2013).

HNCO – Hydrogen isocyanate (isocyanic acid) might possibly be made by irradiating solid N_2 + acetone, but a small abundance is expected. (i) An arrow in Fig. 2(b) of dB18 marks a feature assigned to HNCO, but it points only to a broad, sloping absorbance. It is the only feature labelled as HNCO and it is not obvious how it was integrated and analysed to give an accurate HNCO abundance. Work by Lowenthal et al. (2002) shows that a strong HNCO infrared band exists near 3200 cm^{-1}, close to where dB18 have a band labelled as HCN in their Fig. 2(a) (see our Fig. A3 for a reference spectrum of HNCO). Note that if HNCO formation is from NH + CO → HNCO then NH must first be made and that NH would also react with the N_2 matrix to give $NH + N_2 \rightarrow HN_3$. Several IR features of HN_3 might contribute to the spectrum of irradiated N_2 + acetone (Dows & Pimentel 1955). (ii) The paper cited by dB18 for the HNCO band strength used does not contain HNCO band-strength measurements, but rather it cites only an indirect determination for a solid sample containing H_2O-ice (van Broekhuizen et al. 2004). A direct measurement giving a different value in an anhydrous ice more relevant to this work is in Lowenthal et al. (2002).

HCN – Hydrogen cyanide also might be made in irradiated N_2 + acetone if a multistep reaction path is invoked. (i) Irradiated acetone will yield CH_4, which is known to make H_2CNN (diazomethane) in $N_2 + CH_4$ ices and from there HCN and HNC are produced (Moore et al. 1965; Moore & Hudson 2003 and references therein). However, the evidence for HCN is weak in the dB18 paper. The authors' table 3 gives an IR position of HCN as 3275 cm^{-1}, but the peak labelled HCN in Fig. 2(a) is near 3230 cm^{-1}. Moreover, the molecule's alleged peak near 2100 cm^{-1} in Fig. 2(b) could be for diazomethane, as noted by the authors. If HCN is formed then

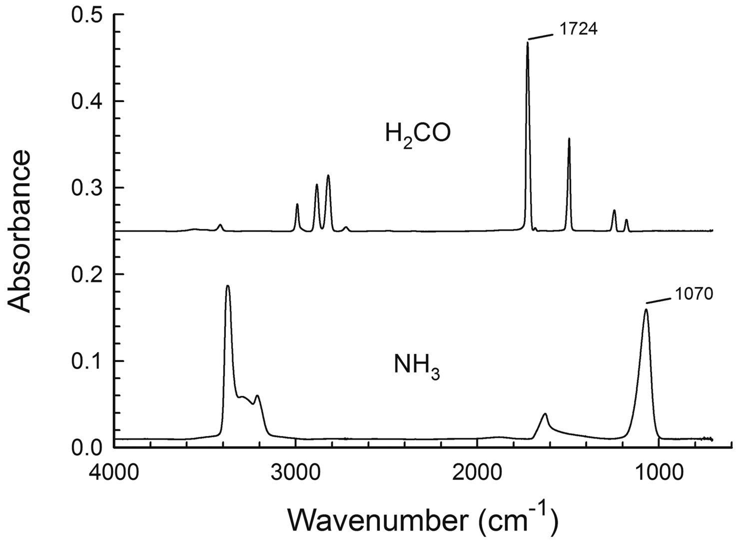

Figure A2. Infrared spectra of amorphous formaldehyde (upper) and ammonia (lower), each ice made and its spectrum recorded near 10 K. Spectra have been offset for clarity (see Gerakines et al. 1996 for the original versions of these spectra).

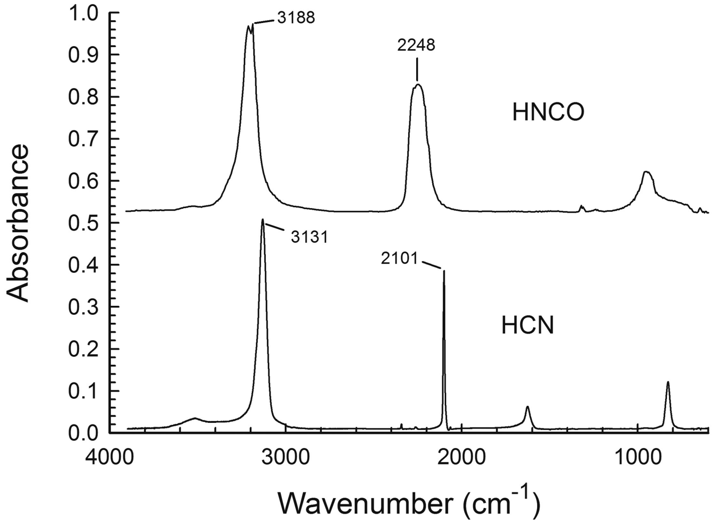

Figure A3. Infrared spectra of amorphous HNCO (upper) at 10 K and amorphous HCN (lower) at 50 K. The HNCO spectrum was digitized from the transmission spectrum of Lowenthal et al. (2002) and the HCN spectrum is from Moore et al. (2010).

one also expects the isomer HNC, but the paper's IR spectra do not show the 3565 cm^{-1} region for HNC's N–H stretching band in N_2 (Milligan & Jacox 1963). No reference spectrum of HCN was shown and so we provide one in Fig. A3. (ii) The band strength estimate in the reference cited by dB18 is from an absorption–reflection experiment and is unlikely to apply to the work of the *MNRAS* authors. A better value can be derived from the optical constants of Moore et al. (2010).

NO – (a) Table 3 of dB18 lists 1875 cm^{-1} as the position of an IR peak of NO, but the authors' Fig. 2(c) labels as NO a small bump, if that, near 1885 cm^{-1}. Also, that same IR feature in the authors' Fig. 2(c) is obscured by the spectrum of the unirradiated ice. The mechanism for NO formation is unclear, and if the molecule is present then it hints at possible contamination of the original ice by atmospheric O_2. Experiments with ^{18}O-labelled acetone would be useful for determining if oxygen-containing contamination is present and for testing the NO assignment. (ii) The band strength listed in table 3 is not from either of the papers cited, but rather it can be traced to a calculation for gas phase NO by Stirling et al. (1994). To our knowledge, this calculated gas phase result has not been compared to a measured solid phase band strength.

NO_2 – (a) Table 3 lists just one peak for NO_2 and in Fig. 2(b) it appears to be only a small bump, if that, on the side of a large sloping feature, making the assignment a weak one. (ii) Again, the correct band-strength reference is Stirling et al. (1994), a calculated gas phase value as opposed to a measured solid phase one.

N_2O_3 – (a) A peak at 1834 cm^{-1} is listed in table 3, but the peak in Fig. 2(c) is closer to 1825 cm^{-1} and seems to be a single point. It is not explained how this small feature was separated from the baseline and accurately integrated. A second feature is labelled N_2O_3 in Fig. 2(c), but is obscured by the spectrum of the unirradiated ice. Once more this must be considered a weak assignment. (ii) The correct band-strength reference is again Stirling et al. (1994), a calculated gas phase value as opposed to a measured solid phase one.

Glycine – There is no single unique IR peak in the paper of dB18 that can be assigned with confidence to glycine. A reference is given for a glycine band strength, again to one of the authors' publications, but a literature search shows that it is taken from a calculation of Holtom et al. (2005) for gas phase glycine.

Conclusion – The infrared assignments for the nine compounds described in this appendix have to be rejected due to the associated IR features not being clearly seen and for lack of supporting data.

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