

# Density functional theory for prediction of far-infrared vibrational frequencies: molecular crystals of astrophysical interest

C. Ennis,<sup>1</sup>★ R. Auchettl,<sup>1</sup> D. R. T. Appadoo<sup>2</sup> and E. G. Robertson<sup>1</sup>

<sup>1</sup>Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Victoria 3086, Australia

<sup>2</sup>Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3148, Australia

Accepted 2017 July 7. Received 2017 July 4; in original form 2017 June 11

## ABSTRACT

Solid-state density functional theory code has been implemented for the structure optimization of crystalline methanol, acetaldehyde and acetic acid and for the calculation of infrared frequencies. The results are compared to thin film spectra obtained from low-temperature experiments performed at the Australian Synchrotron. Harmonic frequency calculations of the internal modes calculated at the B3LYP-D3/m-6–311G(d) level shows higher deviation from infrared experiment than more advanced theory applied to the gas phase. Importantly for the solid-state, the simulation of low-frequency molecular lattice modes closely resembles the observed far-infrared features after application of a 0.92 scaling factor. This allowed experimental peaks to be assigned to specific translation and libration modes, including acetaldehyde and acetic acid lattice features for the first time. These frequency calculations have been performed without the need for supercomputing resources that are required for large molecular clusters using comparable levels of theory. This new theoretical approach will find use for the rapid characterization of intermolecular interactions and bonding in crystals, and the assignment of far-infrared spectra for crystalline samples such as pharmaceuticals and molecular ices. One interesting application may be for the detection of species of prebiotic interest on the surfaces of Kuiper-Belt and Trans-Neptunian Objects. At such locations, the three small organic molecules studied here could reside in their crystalline phase. The far-infrared spectra for their low-temperature solid phases are collected under planetary conditions, allowing us to compile and assign their most intense spectral features to assist future far-infrared surveys of icy Solar system surfaces.

**Key words:** astrochemistry – molecular data – methods: laboratory: molecular – techniques: spectroscopic – Kuiper belt: general – planets and satellites: surfaces.

## 1 INTRODUCTION

Trans-Neptunian Objects (TNOs) have been a target for astronomical research due to their standing as pristine remnants of the proto-solar disc and as chemical time-capsules for organics possibly delivered to Earth during the Late Heavy Bombardment. Near-infrared (NIR) and visible wavelength spectroscopy has been adopted to probe the chemical composition of a number of Centaurs and Kuiper-Belt Objects (KBOs), revealing dominant water (H<sub>2</sub>O) and methane (CH<sub>4</sub>) ice compositions amongst the larger TNOs (Schaller & Brown 2007). More recently, the *New Horizon* spacecraft (Cruikshank et al. 2015; Grundy et al. 2016) located H<sub>2</sub>O, CH<sub>4</sub>, carbon monoxide (CO) and molecular nitrogen (N<sub>2</sub>) ices on Pluto (Owen et al. 1993), while its largest moon Charon displayed patches

of H<sub>2</sub>O, ammonia hydrates and organic materials (Cook et al. 2007). With TNO surface temperatures ranging from 35 to 55 K, the polar components such as H<sub>2</sub>O and ammonia (NH<sub>3</sub>) are locked in as ices, while more volatile species such as CH<sub>4</sub> and N<sub>2</sub> can escape from smaller, airless bodies. This leads to a diversity of chemical environments proposed for various TNOs, which are often classified according to their ‘coloured’ albedos.

Vacuum ultraviolet (UV) photons, solar wind (fast electrons and protons) and cosmic-ray radiation continually impinge on icy TNO surfaces. Irradiation induced chemistry, driven by the production of radicals and ions within the solid-state, is expected to yield higher order molecular products such as carbon dioxide (CO<sub>2</sub>), methanol (CH<sub>3</sub>OH), small hydrocarbons, nitriles and other organic species via non-equilibrium pathways. These processes have been the target of extensive laboratory simulations where molecular ices of various composition have been exposed to UV photolysis and fast particle beams at temperatures (10–150 K) representative of

★ E-mail: c.ennis@latrobe.edu.au

planetary and interstellar ice surfaces (Allodi et al. 2013; Oberg 2016). The identity and formation rates of higher order products are typically verified by online infrared (IR) spectroscopy and mass spectrometry of desorbed gases. The cumulative outputs of these studies have shown that organic molecules of complexity up to amino acids, nucleobases, polyaromatic hydrocarbons and extended nitrogenous polymers (tholins) can be produced at low temperature; given that the correct molecular precursors, sufficient dosage and a suitable substrate/ice morphologies are present.

Once formed in the outer Solar system, there is evidence that higher order products seeded within ice matrices can segregate into multi component polar and non-polar domains, or even pure crystalline material, if sufficiently high abundances and annealing conditions allow. Formally, the thermal energy that is required to overcome diffusion barriers and rearrange disordered ice structure is unavailable at temperatures less than 50 K. However, micrometeorite impacts, cryovolcanism, tidal heating, and the radiogenic decay of mineral isotopes are some non-equilibrium processes that could feasibly act to anneal astronomical ices (Dumas et al. 2011). Evidence for such annealing processes has been inferred on TNO Haumea (Merlin et al. 2007) and KBO Quaoar (Jewitt & Luu 2004) by the detection of the 1.65  $\mu\text{m}$  cubic water ice feature. These findings suggest that the amorphous solid water to crystalline water transition, typically observed between 120 and 140 K in the laboratory, also unfolds on cold, distant TNO surfaces.

Crystal-phase ices such as  $\text{CO}_2$ , hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{CH}_3\text{OH}$ , formaldehyde ( $\text{H}_2\text{CO}$ ), acetaldehyde ( $\text{CH}_3\text{CHO}$ ), formic acid ( $\text{HCOOH}$ ) and acetic acid ( $\text{CH}_3\text{COOH}$ ) – all of which can be formed via sequential recombination or hydrogenation reactions between the reactive products of  $\text{H}_2\text{O}/\text{CH}_4/\text{CO}$  ice irradiation – have yet to be identified on TNO surfaces. This is mostly due to the limited ability of remote NIR and visible telescopes to identify abundances of trace constituents amongst more dominant components. To overcome these limitations, future spacecraft missions could implement far-infrared (far-IR or THz region) spectroscopy to interrogate TNO ices; operating in a similar manner that the Composite Infrared Spectrometer (CIRS) on board the *Cassini* spacecraft to Saturn (Flasar et al. 2004). Here, the CIRS instrument obtained detailed spectra of hydrocarbon and nitrile species in the Titan atmosphere, as well as observing absorption bands attributed to crystalline-phase aerosol particles in the lower atmosphere (de Kok et al. 2007).

Intermolecular lattice bands associated with molecular crystals are generally weaker in intensity than the fundamental vibrations that populate the mid-IR and NIR regions. However, lattice features can provide additional information on the physical ice environment; often showing temperature and morphology dependent band profiles and positions. Far-IR features can also be used to determine chemical composition, which can be of particular use for dense atmospheres and heterogeneous surfaces otherwise completely saturated in congested mid-IR regions. For example, mid-IR features for solid acetonitrile and propionitrile share common fundamental CN and CH stretching frequencies. However, their far-IR ice features are distinct and have been used to confirm their presence in mixed nitrile ices (Ennis et al. 2017).

In this study, we aim to develop a methodology to predict the far-IR signatures of molecular crystals of astrochemical interest. This data could be used to assist detection of higher order organic products in distant Solar system environments where, as opposed to mid- and NIR measurements, there are comparatively few experimental studies on molecular ices in the far-IR region. In addition, the literature is devoid of theoretical studies concerning the vibrational

spectra of these systems, presumably due to the high computational demands of *ab initio* calculations applied to large molecular clusters and bulk ice systems. Therefore, we apply Density Functional Theory (DFT) by way of a periodic boundary approach to optimize molecular crystal structures to obtain simulated vibrational spectra at reduced computational cost. The molecular ice targets of interest include  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$  – three higher order organics that have been experimentally verified as products of irradiated  $\text{H}_2\text{O}/\text{CH}_4/\text{CO}$  ice mixtures, representative of TNO surfaces (Moore & Hudson 1998; Bennett et al. 2005; Bennett & Kaiser 2007; Kaiser, Maity and Jones 2014). Finally, the far-IR spectra generated from these calculations were compared to molecular thin film experiments performed with a new low-temperature system installed at the Australian Synchrotron.

## 2 EXPERIMENTAL

### 2.1 Computational details

The computational approach applied in this study follows the methodology of Civalieri, Doll and Zicovich-Wilson (2007), and references therein. Here, the authors employed a development version of the CRYSTAL code to perform structure optimization and cohesive energy calculations for crystalline urea, allowing Hamiltonian and basis set combinations to be benchmarked against experimental data. Urea has been used as a prototype molecular crystal for periodic *ab initio*, DFT and hybrid methods over the previous decades (Dovesi et al. 1990). Although, some deviation from experimental lattice parameters and cell volumes were observed at the B3LYP/6–31G(d, p) level in the earlier study, we selected the B3LYP functional in this current work due to the ubiquity of B3LYP in the astrochemical literature. For C and O atoms, we implement the m-6–311G(d) split-valence, triple- $\zeta$  basis set of Heyd et al. (2005), where diffuse functions – considered redundant for the solid state – are omitted. H atoms were described by the 3–1p1G basis set of Gatti, Saunders and Roetti (1994), as employed previously for crystalline urea. All basis sets were directly transcribed to the CRYSTAL14 (C14) input files from the online CRYSTAL Basis Sets Library. Also note that dispersion interactions – critical to adequately describe intermolecular forces in crystal systems – were not incorporated in earlier versions of CRYSTAL. However, with the recent inclusion of Grimme’s empirical correction terms for dispersion in the C14 code (denoted as -D3 herein; Grimme 2006) deviation from experiment is expected to be significantly reduced compared to earlier studies (Dovesi et al. 2014).

For molecular crystals modelled in this study, solid-state information was obtained from crystallographic information files (CIFs) sourced from online databases. CIFs contain all necessary data (Table 1) required to write C14 input files (.d12); including crystal space group, lattice parameters and fractional atomic coordinates. For the  $\text{CH}_3\text{OH}$  (Torrie et al. 2002),  $\text{CH}_3\text{CHO}$  (Ibberson, Yamamuro and Matsuo 2000) and  $\text{CH}_3\text{COOH}$  (Albinati et al. 1978) low-temperature solids, crystallographic data were obtained from neutron diffraction experiments performed on their deuterated analogues, where hydrogen atoms were then directly substituted into the unit cell D-coordinates for optimization. Geometry optimization for the periodic crystal system was then initiated with the SCF convergence threshold set to default  $10^{-7}$  au and the shrinking factor for the reciprocal space net set to 3. Coulomb and exchange series tolerances were set as  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-9}$  and  $10^{-30}$ , as recommended for the m-6–311G(d) basis set. Grimme’s dispersion corrections used a scaling factor of 1.05, steepness of 20 and a cut-off

**Table 1.** C14 diffraction data inputs and optimized lattice parameters.

|                              | Temperature (K) | Space group                                     | Z | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | Volume (Å <sup>3</sup> ) | Density (g cm <sup>-3</sup> ) | CIF      |
|------------------------------|-----------------|-------------------------------------------------|---|--------------|--------------|--------------|--------------------------|-------------------------------|----------|
| $\alpha$ -CH <sub>3</sub> OH |                 |                                                 |   |              |              |              |                          |                               |          |
| Diffraction <sup>a</sup>     | 160             | <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i> | 4 | 4.94         | 4.65         | 9.11         | 209.73                   | 1.020                         | 591 0013 |
| Calculated                   |                 |                                                 |   | 4.87         | 4.64         | 8.87         | 200.53                   | 1.061                         |          |
| Deviation (%)                |                 |                                                 |   | 1.36         | 0.19         | 2.67         | 4.39                     | -4.02                         |          |
| $\beta$ -CH <sub>3</sub> OH  |                 |                                                 |   |              |              |              |                          |                               |          |
| Diffraction <sup>b</sup>     | 160             | <i>Cmc2<sub>1</sub></i>                         | 4 | 6.40         | 7.22         | 4.65         | 214.76                   | NA                            | 0701 877 |
| Calculated                   |                 |                                                 |   | 6.40         | 7.31         | 4.57         | 213.72                   | 0.995                         |          |
| Deviation (%)                |                 |                                                 |   | 0            | -1.25        | 1.72         | 0.48                     | -                             |          |
| CH <sub>3</sub> CHO          |                 |                                                 |   |              |              |              |                          |                               |          |
| Diffraction <sup>c</sup>     | 5               | <i>P2<sub>1</sub>/c</i>                         | 4 | 3.91         | 5.42         | 12.20        | 257                      | NA                            | NA       |
| Calculated                   |                 |                                                 |   | 3.91         | 5.42         | 12.19        | 257.44                   | 1.572                         |          |
| Deviation (%)                |                 |                                                 |   | 0.08         | -0.04        | 0.11         | -0.17                    | -                             |          |
| CH <sub>3</sub> COOH         |                 |                                                 |   |              |              |              |                          |                               |          |
| Diffraction <sup>d</sup>     | 12.5            | <i>Pna2<sub>1</sub></i>                         | 4 | 13.20        | 3.89         | 5.76         | 289.19                   | 1.471                         | 2008 187 |
| Calculated                   |                 |                                                 |   | 13.13        | 3.85         | 5.72         | 289.23                   | 1.378                         |          |
| Deviation (%)                |                 |                                                 |   | 0.55         | 1.03         | 0.64         | -0.02                    | 6.32                          |          |

Notes. <sup>a</sup>Torrie et al. (2002).

<sup>b</sup>Ice density not available.

<sup>c</sup>Ice density and CIF not available.

<sup>d</sup>Albinati et al. (1978).

distance of 25, with conventional  $C_6$  and  $R_{vdw}$  parameters applied for H, C and O atoms. Upon completion, the optimized unit cell volumes provided in the output file were compared to experiment (Table 1). Here, only a slight overestimation for CH<sub>3</sub>CHO (0.17 per cent) and CH<sub>3</sub>COOH (0.02 per cent) volumes were observed, while the  $\alpha$ -CH<sub>3</sub>OH volume was underestimated by 4.39 per cent, due to derivation of contracted *a* and *c* lattice parameters. Visual inspection of the lattice network was performed using the MOLDRAW package (Ugliengo, Viterbo and Chiari 1993) at each optimization step. The lowest energy molecular lattice was then exported in CIF format for presentation of the  $\alpha$ -CH<sub>3</sub>OH (Fig. S1),  $\beta$ -CH<sub>3</sub>OH (Fig. S2), CH<sub>3</sub>CHO (Fig. S3) and CH<sub>3</sub>COOH (Fig. S4) crystal structures using the MERCURY CSD 3.9 software. These are included in the online supporting information.

Vibrational frequency calculations were performed on the optimized molecular crystals following the CRYSTAL methodology as detailed by Pascale et al. (2004), implementing the default SCF convergence criterion of  $10^{-9}$  au. Harmonic frequencies were computed with IR intensities (INTENS) calculated by a Berry phase approach (INTPOL), to generate data tables (IRSPEC) for the simulation of IR spectra. Each output file was checked to ensure no negative frequencies were returned with only three crystal translation modes (0 cm<sup>-1</sup>). Molecular displacement analysis was performed to determine the intermolecular and intramolecular character of each specific vibration. The frequency, symmetry species, IR and Raman activity, IR intensity and vibrational assignments calculated by periodic-DFT for solid  $\alpha$ -CH<sub>3</sub>OH (Table S1), CH<sub>3</sub>CHO (Table S2) and CH<sub>3</sub>COOH (Table S3) are compiled in the online supporting information.

## 2.2 Methanol benchmarks

Vibrational frequencies calculated for  $\alpha$ -CH<sub>3</sub>OH solid (Fig. S1), using the periodic DFT method at the B3LYP-D3/m-6-311G(d) level, were compared to frequencies for the isolated, gas-phase CH<sub>3</sub>OH molecule (Table 2). Gas-phase frequencies were calculated using semi-empirical DFT functionals commonly compared to experimental IR spectra; B3LYP-D3 and wB97XD (both

including Grimme's correction for dispersion), as well as the *ab initio* methods MP2 and CCSD. For these functionals, we incorporate the triple- $\zeta$  plus polarization (TZP) basis sets of Pople (6-311G(d): for direct comparison to C14 calculations) and of Dunning (aug-cc-pVTZ: diffuse functions included). All gas-phase calculations are performed using the Gaussian09 (G09) quantum chemistry package accessed through the Australian National Computing Infrastructure (NCI); employing 16 processors in parallel. Anharmonic calculations are performed at the B3LYP-D3/6-311G(d) and B3LYP-D3/aug-cc-pVTZ levels using the generalized second-order vibrational perturbation theory (2VPT) approach implemented by G09.

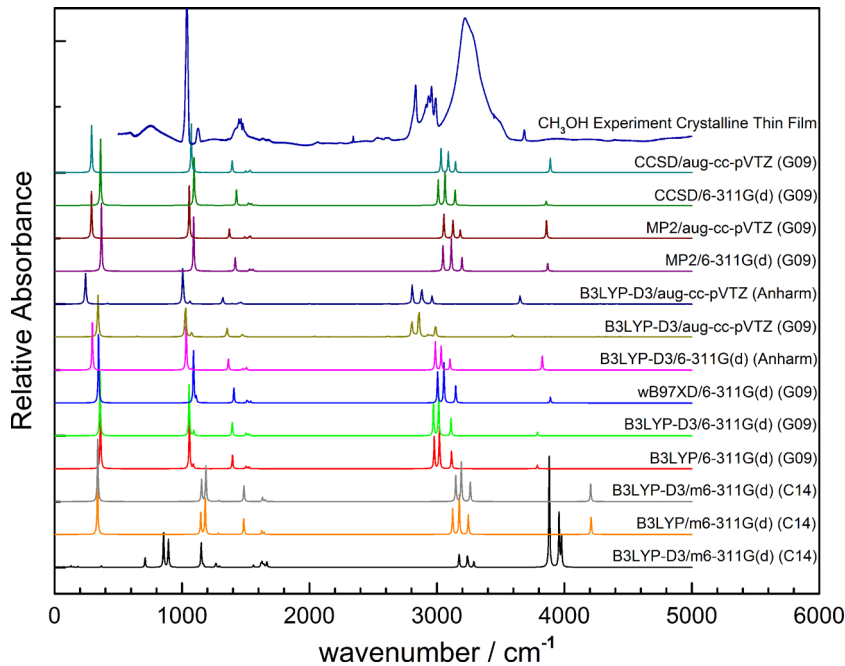
First, it is evident that C14 B3LYP-D3/m-6-311Gd calculations for the isolated CH<sub>3</sub>OH molecule (Fig. 1) return higher frequencies than those identified from gas-phase experiments (Table 2) (Shimanouchi 1977). For example, the three gas-phase C–H stretching peaks at 2844 ( $\nu_3$ ), 2960 ( $\nu_9$ ) and 3000 cm<sup>-1</sup> ( $\nu_2$ ) are calculated by C14 to reside at 3124, 3175 and 3246 cm<sup>-1</sup>, respectively. Here, an average C14 to experiment scaling factor of 0.91 is derived by averaging the fundamental deviations. As also seen in Fig. 1, the isolated CH<sub>3</sub>OH frequencies calculated from the C14 experiments are significantly blue-shifted when compared to all other theories, particularly when compared to the accurate but high-cost anharmonic calculations. These discrepancies persist even when applying the same C14 functional/basis set combinations for harmonic frequency calculations using G09; with deviations appearing to increase with the higher frequency C–H and O–H stretching modes. These comparisons between methods indicate that C14 is not the most accurate tool for the single, gas-phase molecule.

The crystalline  $\alpha$ -CH<sub>3</sub>OH spectrum produced from the periodic-DFT calculations is depicted as the lower spectrum in Fig. 1, where it can be compared to the two C14 CH<sub>3</sub>OH monomer spectra shown directly above. Here, we observe the expected redshift for the O–H stretching mode induced by strong hydrogen-bonding interactions in the crystalline phase. The calculated shift of -285 cm<sup>-1</sup> is considerably smaller than that observed in experiment (-476 cm<sup>-1</sup>), although the broad profile of the thin film peak introduces error

**Table 2.** C14 to experiment scaling factors for gas-phase CH<sub>3</sub>OH and the crystalline-phase solid.

| CH <sub>3</sub> OH mode             | Gas-phase/monomer                           |                         |                | Crystalline $\alpha$ -phase solid |                         |                |
|-------------------------------------|---------------------------------------------|-------------------------|----------------|-----------------------------------|-------------------------|----------------|
|                                     | Experiment (cm <sup>-1</sup> ) <sup>a</sup> | C14 (cm <sup>-1</sup> ) | Scaling factor | Experiment (cm <sup>-1</sup> )    | C14 (cm <sup>-1</sup> ) | Scaling Factor |
| $\nu_1$ (OH stretch)                | 3681                                        | 4209                    | 0.88           | 3205                              | 3883–3963               | 0.84           |
| $\nu_2$ (CH <sub>3</sub> stretch)   | 3000                                        | 3246                    | 0.92           | 2981                              | 3285                    | 0.91           |
| $\nu_9$ (CH <sub>3</sub> stretch)   | 2960                                        | 3175                    | 0.93           | 2940                              | 3241                    | 0.91           |
| $\nu_3$ (CH <sub>3</sub> stretch)   | 2844                                        | 3124                    | 0.91           | 2926                              | 3177                    | 0.92           |
| $\nu_4$ (CH <sub>3</sub> deform)    | 1477                                        | 1644                    | 0.90           | 1475                              | 1666                    | 0.89           |
| $\nu_{10}$ (CH <sub>3</sub> deform) | 1477                                        | 1629                    | 0.91           | 1459                              | 1645                    | 0.89           |
| $\nu_5$ (CH <sub>3</sub> deform)    | 1455                                        | 1625                    | 0.90           | 1445                              | 1622                    | 0.89           |
| $\nu_6$ (OH bend)                   | 1345                                        | 1485                    | 0.91           | 1420(sh)                          | 1562                    | 0.91           |
| $\nu_{11}$ (CH <sub>3</sub> rock)   | 1165                                        | 1286                    | 0.91           | –                                 | 1293                    | –              |
| $\nu_7$ (CH <sub>3</sub> rock)      | 1060                                        | 1183                    | 0.90           | 1124                              | 1265                    | 0.89           |
| $\nu_8$ (CO stretch)                | 1033                                        | 1147                    | 0.90           | 1026                              | 1150                    | 0.89           |
| $\nu_{12}$ (torsion)                | 295                                         | 337                     | 0.88           | 736 (632–948)                     | 855 (710–890)           | 0.85           |
| Lattice $L$ (B1)                    | –                                           | –                       | –              | 343                               | 368                     | 0.92           |
| <b>Average</b>                      |                                             |                         | <b>0.91</b>    |                                   |                         | <b>0.90</b>    |

Note. <sup>a</sup>Shimanouchi (1977) located on NIST Chemistry Webbook data.



**Figure 1.** Simulated IR spectra from calculations on the isolated CH<sub>3</sub>OH molecule using various methods available with the C14 (second and third from the bottom) and G09 packages. These are compared to calculations for the crystalline molecular solid (bottom) at C14 B3LYP-D3/m-6–31G(d) level of theory. Mid-IR spectra for the crystalline CH<sub>3</sub>OH thin film experiment at 120 K (top).

to the measurement (Table 2). Otherwise, the  $\alpha$ -CH<sub>3</sub>OH spectrum indicates significant shifts for the deformation and bending modes located in the 800–1700 cm<sup>-1</sup> region, compared to the monomer spectra. These assignments will be discussed in greater detail in the following sections.

Compared to the CH<sub>3</sub>OH thin film experiment, shown as the uppermost spectrum in Fig. 1, the C14  $\alpha$ -CH<sub>3</sub>OH calculations also overestimate all fundamental frequencies, as previously observed with the gas-phase calculations. Measuring to the peak maxima of the broad experimental peaks, the calculated O–H stretch region is positioned some 700 cm<sup>-1</sup> to higher frequency, resulting in a large scaling factor of 0.84. Otherwise, the remaining fundamentals show deviations in the range of 0.89–0.92 across the mid-IR region. However, improvement in accuracy for intermolecular lattice modes is alluded to with the 0.92 scaling factor derived for the intense

libration (B1) band calculated at 368 cm<sup>-1</sup> – observed at 343 cm<sup>-1</sup> in the thin film experiment.

Gas-phase calculations across all levels of theory are consistent in showing the  $\nu_{12}$ (torsion) at  $\sim 360$  cm<sup>-1</sup> and the  $\nu_8$ (C–O stretch) at  $\sim 1050$  cm<sup>-1</sup> are the fundamental modes possessing the bands of highest intensity. The main differences in calculated band intensity between the CH<sub>3</sub>OH monomer and the  $\alpha$ -CH<sub>3</sub>OH crystal spectra concern the C–H stretching modes, as well as the relative strength of the  $\nu_1$ (O–H stretch) mode. Upon crystallization to bulk  $\alpha$ -CH<sub>3</sub>OH, the periodic DFT calculations predict the O–H stretching mode to split into three intense peaks (representing B3, B1 and B2 symmetry in P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) that dominate the mid-IR spectra between 3880 and 3970 cm<sup>-1</sup>. Periodic DFT calculations also predict a pronounced shift for the  $\nu_{12}$ (torsion) mode upon crystallization. Calculated to lie at  $\sim 360$  cm<sup>-1</sup> in the gas-phase, formation of  $\alpha$ -CH<sub>3</sub>OH sees

the frequency of the three IR active modes (of different symmetry species) to be blue-shifted to 710 (B3), 855 (B1) and 890 (B2)  $\text{cm}^{-1}$ . Normal mode analysis of the  $\text{CH}_3\text{OH}$  displacements in the unit cell allude to the hydrogen-bonding in the crystalline solid as the reason for this considerable shift in the  $\nu_{12}$ (torsion) mode. Torsional motion often presents a challenge for harmonic frequency calculations due to highly anharmonic potentials, large amplitude motions and tunnelling involving hydrogen atoms. It is presumed that the adequate prediction for crystalline  $\text{CH}_3\text{OH}$  is at least partly due to fortuitous cancelation of errors using DFT theory.

### 2.3 Thin film spectroscopy

Thin films of molecular ices were produced at the far-IR and THz Beamline at the Australian Synchrotron using an apparatus recently constructed for transmission and reflection–absorption infrared spectroscopy (RAIRS) experiments. A stainless steel high-vacuum chamber (base pressure  $2 \times 10^{-8}$  Torr) housing a closed-cycle helium cryocooler (Sumitomo CH202) was lowered into the sample compartment of the beamline spectrometer (Bruker IFS125). Here, the copper target holds an IR transparent window for cooling to 20 K with the temperature measured by a silicon diode sensor (Lakeshore). Volumes of 5 mL of the sample liquids ( $\text{CH}_3\text{OH}$ : Sigma Anhydrous 99.8 per cent;  $\text{CH}_3\text{CHO}$ : Sigma Anhydrous  $\geq 99.5$  per cent;  $\text{CH}_3\text{COOH}$ : Sigma ACS  $\geq 99.7$  per cent) were transferred to glass ampoules for removal of trapped volatiles by the freeze–pump–thaw procedure. The vapour was then collected and transferred for vacuum deposition, performed over 2–5 min at a chamber background pressure of  $\sim 5 \times 10^{-4}$  Torr. The film thickness was controlled as to ensure amorphous lattice features absorbed a maximum of  $\sim 50$  per cent of the radiation across all wavelengths. This limit was imposed to prevent saturation of intense crystalline features upon warming.

All spectra were collected in transmission mode using IR transparent windows as deposition substrates. Polyethylene was used for the outer chamber windows, while  $10 \times 1.5$  mm silicon wafers (Edmund) was used for the far-IR substrate. For mid-IR measurements, KBr was used as the window material throughout. The substrates were rotated normal to the optical axis of the spectrometer for deposition (background vapour deposition). Far-IR spectra required use of a  $5 \mu\text{m}$  Mylar beamsplitter, the synchrotron radiation source and a liquid-He cooled bolometer to access the  $50$ – $600 \text{ cm}^{-1}$  region. Mid-IR measurements employed a KBr beamsplitter, an internal Global source and a liquid-N<sub>2</sub> cooled MCT detector to access the  $500$ – $5000 \text{ cm}^{-1}$  region. All presented spectra were recorded at  $4 \text{ cm}^{-1}$  resolution and were averaged from 20 individual scans.

Our experimental ice thickness could be estimated by performing mid-IR experiments on  $\text{CH}_3\text{OH}$  thin films generated under identical deposition conditions. Here, we determined that our mid-IR  $\text{CH}_3\text{OH}$  films were of the order of  $450 \pm 50 \text{ nm}$ ; calculated using the literature  $\text{CH}_3\text{OH}$   $\alpha$ -phase density of  $1.02 \text{ g cm}^{-3}$  (Tauer & Lipscomb 1952) and the absorption coefficients (A-values) for five isolated fundamental absorption features across the mid-IR spectrum (Palumbo, Castorina and Strazzulla 1999). The far-IR thin films were formed at  $8\times$  longer deposition time (compared to the mid-IR deposition) to yield observable lattice features. We extrapolate the far-IR film thicknesses to be of the order of  $3$ – $4 \mu\text{m}$ . Controlled heating of the thin films was performed from the 20 K base deposition temperature to the desorption temperature under high vacuum conditions for the specific molecular ice. This was performed using a Lakeshore 330 temperature controller connected to a  $50 \Omega$  resistive heater, with proportional–integral–derivative

settings programmed for a linear  $0.5 \text{ K min}^{-1}$  temperature ramp. Spectra were collected at every 2 K temperature step.

## 3 RESULTS AND DISCUSSION

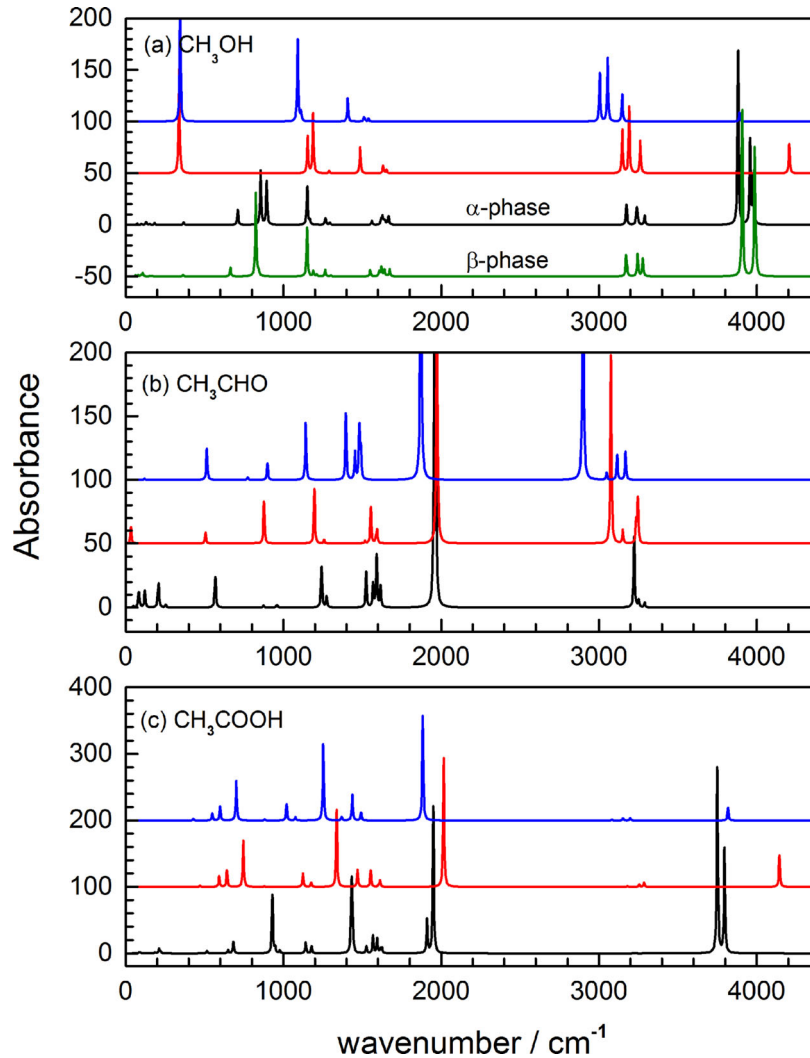
### 3.1 Methanol ( $\text{CH}_3\text{OH}$ )

Solid  $\text{CH}_3\text{OH}$  has two stable phases below its 180 K melting point (Tauer & Lipscomb 1952). Upon cooling the liquid, the  $\beta$ -phase solid is first observed in the narrow temperature range of  $170$ – $180 \text{ K}$  (Fig. S2); displaying hydrogen bonding linkages down the  $a$ -coordinate. Below  $170 \text{ K}$ , a transition to the  $\alpha$ -phase (Fig. S1) sees the unit cell volume decrease as neighbouring methyl groups rotate toward closer contact but maintaining the directionality of the hydrogen bonds. Annealing amorphous thin films from low temperature is expected to undergo transformation to the  $\alpha$ - $\text{CH}_3\text{OH}$  structure at around  $130 \text{ K}$  (Torrie et al. 2002). To ensure that the  $\alpha$ - $\text{CH}_3\text{OH}$  structure was indeed the crystalline form in the present experiments, we calculated both crystalline phases; the  $\alpha$ - $\text{CH}_3\text{OH}$  phase from data extracted from the neutron powder study of Torrie et al. (2002) and the  $\beta$ - $\text{CH}_3\text{OH}$  phase from data obtained from Kirchner, Das and Boese (2008). Comparison of the simulated spectra of both crystalline phases (Fig. 2a) to experimental mid-IR spectra (Fig. 1: top spectrum) suggests that the  $\alpha$ - $\text{CH}_3\text{OH}$  has been formed as expected, after annealing the amorphous ice to  $120 \text{ K}$  under our experimental conditions.

Far-IR studies of pure  $\text{CH}_3\text{OH}$  thin films were first performed by Moore and Hudson (1994) covering the  $100$ – $500 \text{ cm}^{-1}$  region. The amorphous-phase ice deposited at  $20 \text{ K}$  showed a prominent peak at  $148 \text{ cm}^{-1}$  with a broad shoulder extending to  $320 \text{ cm}^{-1}$ . Upon annealing the ice to  $100$ – $120 \text{ K}$ , a series of resolved absorption bands were identified at  $113$ ,  $147$  and  $175 \text{ cm}^{-1}$ ; in addition to a narrow, intense band at  $353 \text{ cm}^{-1}$  to confirm the transition to crystalline material. THz spectra recorded by Ioppolo et al. (2014) indicate that amorphous-phase  $\text{CH}_3\text{OH}$  is formed by deposition at  $10 \text{ K}$  by two broad, unresolved features spanning  $50$ – $120$  and  $130$ – $200 \text{ cm}^{-1}$ . Transition to crystalline  $\alpha$ - $\text{CH}_3\text{OH}$  was observed at  $140 \text{ K}$  before re-cooling to  $10 \text{ K}$ . The THz spectra of the crystalline phase shows five peaks at  $70$ ,  $90$ ,  $115$ ,  $145$  and  $180 \text{ cm}^{-1}$ , while a baseline inflection suggests an intense feature is positioned beyond the  $250 \text{ cm}^{-1}$  limit.

The amorphous phase  $\text{CH}_3\text{OH}$  formed in this study (Fig. 3a) resembles the amorphous ice of Moore and Hudson (1994), where we observe a broad feature peaking at  $140 \text{ cm}^{-1}$  with a shoulder extending out to  $325 \text{ cm}^{-1}$  (Table 3). The amorphous ice remains unchanged to  $105 \text{ K}$ , after which a phase transition to the  $\alpha$ -phase takes place. Here, two rather broad and weak features appear at  $103$  and  $163 \text{ cm}^{-1}$ , while a third peak is identified at  $56 \text{ cm}^{-1}$  close to the low-frequency limit of the experimental setup. The emergence of these peaks coincides with the appearance of a narrow, intense feature at  $343 \text{ cm}^{-1}$  that becomes saturated by  $120 \text{ K}$ . Most bands appear redshifted  $\sim 10$ – $20 \text{ cm}^{-1}$  from the positions detailed by Moore and Hudson (1994). Extending to  $30 \text{ cm}^{-1}$ , the THz spectra presented by Ioppolo et al. (2014) are richer in features, with additional strong bands located at  $70$  and  $90 \text{ cm}^{-1}$ . However, corresponding peaks are not evident in our spectra, possibly hidden due to noise in the immediate  $80 \text{ cm}^{-1}$  region observed in this experiment.

However, the simulated spectra derived from periodic DFT calculations on  $\alpha$ - $\text{CH}_3\text{OH}$  (Fig. 3a) –after application of the 0.92 scaling factor – compare favourably with the THz spectra presented by



**Figure 2.** Simulated IR spectra from calculations on the crystalline molecular solid (bottom –black/green) and the isolated molecule (middle – red) at C14 B3LYP-D3/m-6–311G(d) level of theory for (a)  $\alpha$ - &  $\beta$ -CH<sub>3</sub>OH, (b) CH<sub>3</sub>CHO and (c) CH<sub>3</sub>COOH. Also included are B3LYP-D3/6–311G(d) calculations for the isolated monomer using the Gaussian 09 package (top – blue).

Ioppolo et al. (2014). The five distinct experimental peaks clearly resolved below 200 cm<sup>-1</sup> can be directly assigned to the lattice features calculated at 68, 92, 120, 140 and 170 cm<sup>-1</sup>, which are a mixture of translation and libration contributions with highest calculated intensity (Table 3). However, the intense lattice feature predicted at 339 cm<sup>-1</sup> (B<sub>1</sub>) deviates by ~15 cm<sup>-1</sup> from the intense absorption band displayed at 353 cm<sup>-1</sup> in the spectrum of Moore and Hudson (1994). The lower frequency lattice features of our CH<sub>3</sub>OH ice are broader and redshifted compared to the two literature results. Not appearing to align with calculated values as closely as the literature spectra, an impurity molecule could be present in sufficient abundance to disrupt the crystalline solid. Water would be the obvious contaminant, although its perceived abundance is not sufficient to show any of its distinct signatures in the mid-IR spectrum.

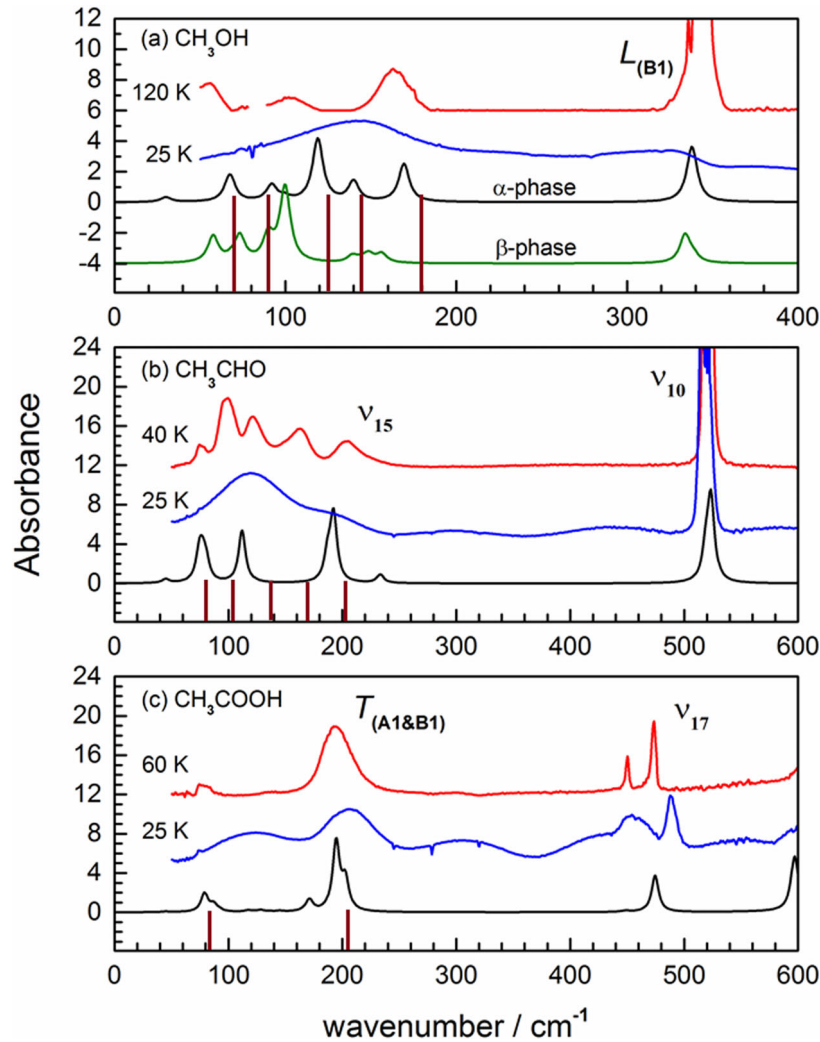
### 3.2 Acetaldehyde (CH<sub>3</sub>CHO)

Solid CH<sub>3</sub>CHO displays a stable, monoclinic (*P*2<sub>1</sub>/*c*) crystalline structure at low temperature, with a second metastable, orthorhombic-phase only previously identified across a narrow tem-

perature range below its 152 K melting point (Ibberson, Yamamuro and Matsuo 2000). Here, we expect to observe only the stable crystalline phase formed after annealing the 20 K amorphous solid to its ~50 K phase-transition temperature. The structure optimization of crystalline CH<sub>3</sub>CHO converged to produce lattice parameters and unit cell volumes close to those determined by diffraction experiments (Table 1). A visualization of the crystalline structure of CH<sub>3</sub>CHO can be observed in Fig. S3 in the online supporting information.

IR lattice features for crystalline CH<sub>3</sub>CHO had not been investigated prior to the THz investigations of Ioppolo et al. (2014). Here, sub-10- $\mu$ m thick films deposited directly at 10 K produced two broad absorption features centred at 117 and 200 cm<sup>-1</sup> attributed to the amorphous solid. For films deposited at 125 K before cooling to 10 K, crystalline-phase absorption bands were identified at 80, 105, 135, 170 and 205 cm<sup>-1</sup> (Fig. 3b: stick spectra). All bands are clearly resolved with symmetric band profiles. Annealing the CH<sub>3</sub>CHO amorphous ice film confirmed a 70 K crystallization temperature by the emergence of the five sharp crystalline features.

CH<sub>3</sub>CHO thin films produced in this study are consistent with those produced in the THz study (Table 3). Immediately, after



**Figure 3.** Simulated far-IR spectra for (a)  $\alpha$ -CH<sub>3</sub>OH &  $\beta$ -CH<sub>3</sub>OH, (b) CH<sub>3</sub>CHO and (c) CH<sub>3</sub>COOH crystalline solids as calculated by C14 B3LYP-D3/m-6-311G(d) with a 0.92 scaling factor applied (bottom – black/green). Synchrotron thin-film far-IR spectra for the low-temperature amorphous solid (middle – blue) and the annealed crystalline-phase solid (top – red). Stick spectra for the experimental THz band positions from Ioppolo et al. (2014) are included for reference (burgundy).

deposition at 20 K, the amorphous structure of CH<sub>3</sub>CHO (Fig. 3b) is identified by the intense, broad absorption feature with maximum intensity at 120 cm<sup>-1</sup> that extends out towards 240 cm<sup>-1</sup> (including shoulder at 195 cm<sup>-1</sup>); consistent with the overlap of both amorphous signatures in the THz spectra. At higher frequencies, an extremely strong (saturated) band is identified at 520 cm<sup>-1</sup>, which can be assigned to the  $\nu_{10}$ (CCO deformation) fundamental mode. Upon crystallization, towards low wavenumber, we identify five peaks at 74, 96, 120, 162 and 202 cm<sup>-1</sup>; all clearly resolved and within  $\sim 15$  cm<sup>-1</sup> of the THz film positions. The most interesting discrepancy between the studies is the phase-transition temperature, which was observed in the THz study at  $\sim 70$  K. Surprisingly, we observed the crystalline peaks emerging at a considerably low 35 K, before reaching maximum absorption at 45 K under our experimental conditions.

The simulated IR spectra from C14 calculations on solid CH<sub>3</sub>CHO are not as a convincing factor to experiment as seen previously for CH<sub>3</sub>OH (Fig. 3b), even after introducing the 0.92 scaling factor to calculated frequencies. From analysis of the calculated atomic displacements, the three lowest frequency bands at 45, 77 and 112 cm<sup>-1</sup> are predominantly translational lattice modes,

while the weak band calculated at 233 cm<sup>-1</sup> shows a libration-mode character. The relative intensities for these four lattice modes appear somewhat consistent between theory and crystalline thin film. However, the calculated band positions are spread out over a wider frequency range than experiment with an intensity free window between 130 and 180 cm<sup>-1</sup>. The most intense band in the cluster at 191 cm<sup>-1</sup>, is not attributed to a lattice mode but rather the  $\nu_{15}$ (torsion) mode but this lowest lying fundamental for the CH<sub>3</sub>CHO molecule does not show high intensity in the experimental spectra. Finally, the intense  $\nu_{10}$  vibration mode is calculated to lie at 522 cm<sup>-1</sup>, which shows excellent agreement with the thin film position after applying the 0.92 scaling factor. One could reason that the absence of hydrogen bonding between CH<sub>3</sub>CHO molecules may translate into increased error in calculating intermolecular lattice frequencies.

### 3.3 Acetic acid (CH<sub>3</sub>COOH)

Solid CH<sub>3</sub>COOH displays only the single crystalline-phase at low temperature; belonging to the orthorhombic *Pna*2<sub>1</sub> space group as identified by neutron powder diffraction experiments

**Table 3.** Calculated and experimental far-IR spectral assignments.

| Sample                       | Amorphous  |                  | Crystalline |                                    |                         |                                                                            |
|------------------------------|------------|------------------|-------------|------------------------------------|-------------------------|----------------------------------------------------------------------------|
|                              | Experiment | Literature       | Experiment  | Literature                         | Calculated <sup>e</sup> | Assignment <sup>f</sup>                                                    |
| $\alpha$ -CH <sub>3</sub> OH |            |                  | 56          | 70 <sup>a</sup>                    | 68                      | <i>T</i> (B <sub>1</sub> & B <sub>3</sub> )                                |
|                              |            |                  | 103         | 90 <sup>a</sup>                    | 92                      | <i>T</i> (B <sub>2</sub> ) and <i>L</i> (B <sub>1</sub> & B <sub>2</sub> ) |
|                              |            |                  |             | 115 <sup>a</sup> /113 <sup>b</sup> | 120                     | <i>T</i> (B <sub>1</sub> )                                                 |
|                              | 140        | 148 <sup>b</sup> | 163         | 145 <sup>a</sup> /147 <sup>b</sup> | 140                     | <i>L</i> (B <sub>3</sub> )                                                 |
|                              |            |                  |             | 180 <sup>a</sup> /175 <sup>b</sup> | 170                     | <i>T</i> (B <sub>3</sub> ) and <i>L</i> (B <sub>1</sub> & B <sub>2</sub> ) |
|                              | 325(sh)    | 321 <sup>b</sup> | 343         | 353 <sup>b</sup>                   | 339                     | <i>L</i> (B <sub>1</sub> )                                                 |
| CH <sub>3</sub> CHO          |            |                  |             |                                    | 45                      | <i>T</i> (B <sub>u</sub> , A <sub>u</sub> & B <sub>u</sub> )               |
|                              |            |                  | 74          | 80 <sup>a</sup>                    | 77                      | <i>T</i> (B <sub>u</sub> , A <sub>u</sub> & B <sub>u</sub> )               |
|                              |            |                  | 96          | 105 <sup>a</sup>                   |                         |                                                                            |
|                              | 120        | 117 <sup>a</sup> | 120         | 135 <sup>a</sup>                   | 112                     | <i>T</i> (B <sub>u</sub> , A <sub>u</sub> & B <sub>u</sub> )               |
|                              |            |                  | 162         | 170 <sup>a</sup>                   | 191                     | $\nu_{15}$ (CH <sub>3</sub> ) torsion                                      |
|                              |            | 200 <sup>a</sup> | 202         | 205 <sup>a</sup>                   | 233                     | <i>L</i> (B <sub>u</sub> )                                                 |
| CH <sub>3</sub> COOH         |            |                  | 517/523     | 516/522 <sup>c</sup>               | 522                     | $\nu_{10}$ (CCO) deform                                                    |
|                              |            |                  | 75          | 85 <sup>a</sup>                    | 78                      | <i>T</i> (A <sub>1</sub> & B <sub>1</sub> )                                |
|                              | 205        | 200 <sup>a</sup> | 195         | 210 <sup>a</sup>                   | 193                     | <i>T</i> (A <sub>1</sub> & B <sub>1</sub> )                                |
|                              | 460        | na               | 450         |                                    |                         |                                                                            |
|                              | 490        | na               | 473         | 449 <sup>d</sup>                   | 474                     | $\nu_{17}$ (CCOH) torsion                                                  |
|                              |            |                  | 486         |                                    |                         |                                                                            |

Notes. <sup>a</sup>Toppolo et al. (2014).

<sup>b</sup>Moore and Hudson (1994).

<sup>c</sup>Hollenstein and Gunthard (1971).

<sup>d</sup>Haurie and Novak (1965).

<sup>e</sup>After 0.92 scaling factor applied.

<sup>f</sup>Far-IR assignments from atomic/molecular displacement analysis (supplement tables). *L*: libration, *T*: translation.

(Albinati et al. 1978). The crystalline form exhibits intermolecular hydrogen-bonding along the *c*-coordinate (Fig. S4). This can result in a significant redshift for the O–H stretching band ( $\sim 400$  cm<sup>−1</sup>) as calculated from the free monomer peak position to the crystalline solid (Fig. 2c). The C14 optimized structure displays only 1 per cent deviation from the experimental lattice, as shown by the almost identical cell volume (Table 1).

Similar to CH<sub>3</sub>CHO, crystalline CH<sub>3</sub>COOH had not previously been investigated in the far-IR region until THz studies were performed by Ioppolo et al. (2014) on sub-10- $\mu$ m-thin films. Upon direct deposition at 10 K, a single broad absorption feature is identified between 120 and 240 cm<sup>−1</sup>, with a peak maximum at  $\sim 210$  cm<sup>−1</sup> (Fig. 3c: stick spectra). Annealing the CH<sub>3</sub>COOH ice to its 100 K crystallization temperature before re-cooling to 10 K, sees the broad feature narrow slightly (from 180 to 240 cm<sup>−1</sup>). As opposed to crystalline features for their other molecules, the feature appears non-Gaussian and likely composed of numerous overlapping bands. A very weak band also appears to emerge at 85 cm<sup>−1</sup>.

The CH<sub>3</sub>COOH spectra collected in the present synchrotron experiments are different in appearance. The amorphous-phase thin film also displays a broad absorption. However, this 205 cm<sup>−1</sup> feature spans a narrower region (160–245 cm<sup>−1</sup>) and is more Gaussian than the THz study (Fig. 3c). A sharp, intense peak at 490 cm<sup>−1</sup> with a broad, weak sideband at 460 cm<sup>−1</sup> accompanies the lower frequency band. Annealing the ice sees the 205 cm<sup>−1</sup> band redshift slightly to 195 cm<sup>−1</sup> and double its peak intensity. This band appears decidedly more sharp and ‘crystalline’ than the corresponding THz peak. A weak, low-frequency feature also appears at  $\sim 75$  cm<sup>−1</sup>. Of most interest is the 460 and 490 cm<sup>−1</sup> doublet that undergoes significant alteration upon crystallization at 50 K. Here, both features are observed to diminish in intensity while two, narrow peaks emerge 450 and 473 cm<sup>−1</sup>. The phase transition, as indicated by total loss

of the amorphous bands and stalled growth of the crystalline bands, is completed by 60 K under our chamber conditions.

The recreation of the crystalline CH<sub>3</sub>COOH ice far-IR spectrum using periodic DFT calculations is satisfying. The band profiles of the strong 195 cm<sup>−1</sup> and its 75 cm<sup>−1</sup> peaks in the experimental spectra closely resemble the predicted spectra at 193 and 78 cm<sup>−1</sup>, respectively, after employing the 0.92 scaling factor. Analysis of the atomic displacements borne out of the C14 calculations show both the 78 and 193 cm<sup>−1</sup> bands arise from torsion-like motions between H-bonded CH<sub>3</sub>COOH molecules. In addition, the high-frequency 473 cm<sup>−1</sup> (B<sub>2</sub>) feature in the thin film CH<sub>3</sub>COOH spectra, assigned to the  $\nu_{17}$ (CCO torsion) fundamental mode, is correctly positioned at 474 cm<sup>−1</sup>. However, its neighbouring 486 cm<sup>−1</sup> peak in the experimental spectra – an example of fundamental peak splitting in the crystalline phase—is not predicted to carry intensity. Note also that the lowest lying CH<sub>3</sub>COOH fundamental mode, the  $\nu_{18}$ (CCO torsion) is not predicted to show noticeable IR intensity, thus it is not identified in either the experimental or calculated spectrum. The precision of the C14 simulations in replicating CH<sub>3</sub>COOH thin film far-IR spectra adds further weight that hydrogen-bonded molecular crystals are particularly well treated by this theory. As the number of molecular systems investigated by this process is expanded to include more systems displaying dispersion interactions, we will have a better grasp on this observed correlation.

#### 4 ASTROPHYSICAL IMPLICATIONS

IR astronomy continues to be an active pursuit following a succession of advanced telescopes such as the Infrared Space Observatory (ESA: 1995–98), the Spitzer Space Telescope (NASA: ongoing since 2003) and the Herschel Space Observatory (ESA: 2009–13) over the previous decades. Improvements in detector design and cooling has allowed access to longer wavelengths into the far-IR at

higher sensitivity and for more extended periods in orbit. These developments have enabled new observations of crystalline ices from Solar system, cometary and interstellar sources previously only surveyed by the ground-based NIR telescopes. For example, crystalline water-ice with its distinctive  $63\ \mu\text{m}$  ( $160\ \text{cm}^{-1}$ ) and  $43\ \mu\text{m}$  ( $230\ \text{cm}^{-1}$ ) lattice bands, has been located in protoplanetary discs (McClure et al. 2015; Min et al. 2016). Here, the presence of crystalline water in environments as cold as 10 K has contributed to the debate with regards to annealing and ice segregation processes within cold, interstellar regions. Spitzer studies have also observed crystalline  $\text{CO}_2$ , as well as  $\text{CO}_2$  mixed with in  $\text{H}_2\text{O}$  and  $\text{CO}$  matrices, formed via solid-state grain reactions within young stellar objects (Pontoppidan et al. 2008); although these studies utilized Davydov splitting of the  $670\ \text{cm}^{-1}$  bending mode of  $\text{CO}_2$  to place the assignment. In addition, low-frequency lattice modes have been used to constrain the morphology of minerals identified on cometary bodies, such as the crystalline silicate forsterite, with implications toward the radial chemical composition of the primordial Solar Nebula (Sitko et al. 2011).

IR measurements of Titan have also been carried out with the CIRS instrument on board the *Cassini* spacecraft; the far-IR focal plane detector able to access the  $20\text{--}600\ \text{cm}^{-1}$  region. One of the primary objectives of the mission was to catalogue the molecular ices within the lower stratosphere ( $\sim 0\text{--}100\ \text{km}$  altitude). Here, mixes of condensed-phase hydrocarbons and nitriles are thought the most likely carriers for the broad  $160$  and  $220\ \text{cm}^{-1}$  ‘haystack’ features. However, their profiles have proven difficult to reproduce in the laboratory due to their heterogeneous and composite character (de Kok et al. 2007; Anderson & Samuelson 2011). Otherwise, gas-phase nitriles with abundances coinciding to some extent with polar region UV exposure, have been confirmed by their sharp, low-frequency fundamental bands in CIRS spectra (e.g.  $\text{HC}_3\text{N}$  at  $506\ \text{cm}^{-1}$ ). With intense far-IR lattice bands, such nitriles are likely candidates for haystack contributors. More non-polar hydrocarbon species are expected to condense at slightly colder (lower) altitudes than nitriles. The most abundant hydrocarbons  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  possess weak far-IR features and are not expected to contribute to the haystack feature. However, some substituted acetylenes and polyynes, such as  $\text{C}_3\text{H}_4$  and  $\text{C}_4\text{H}_2$  have been identified by their low lying fundamentals in CIRS data (Teanby et al. 2009) and can be considered potential candidates for haystack molecules.

With a dominant volatile composition of  $\text{N}_2$  and  $\text{CH}_4$ , along with constant irradiation from UV photons and fast particles, the non-equilibrium chemistry of TNOs is expected to closely resemble that of the Titan atmosphere, with a similar suite of molecular products awaiting our detection. The lower temperatures and tenuous atmospheres pertaining to these bodies likely precludes gas-phase detection of these products. Instead, identification of their abundances residing on TNO surfaces may prove more accessible in future surveys. If atmospheric condensation and precipitation of photoproducts (possibly in pure form) is an ongoing process on the larger TNOs, populations could be concentrated on the surface. In this case, annealing processes could convert their ice morphology into the crystalline solid, as has been detected with the dominant water component.

Successful detection of organic products using far-IR wavelengths would be enhanced if the most intense of the product bands were shifted significantly away from the strong  $160$  and  $230\ \text{cm}^{-1}$  water features; instead residing in spectral windows devoid of interfering peaks (note that both  $\text{N}_2$  and  $\text{CH}_4$  ices have weak far-IR features). The thin film experiments (Fig. 3) indicate a number of intense ‘tracer’ peaks that could potentially be used to confirm the presence of these species on a TNO surface. Methanol shows a

strong lattice feature at  $345\ \text{cm}^{-1}$ , which is the highest frequency lattice band calculated across the selected molecules but  $\sim 150\ \text{cm}^{-1}$  lower than most fundamental vibration bands (except the  $\nu_{18}$  torsion band of  $\text{CH}_3\text{COOH}$  at  $\sim 140\ \text{cm}^{-1}$ ). This peak could therefore be considered a convenient tracer for crystal-phase  $\text{CH}_3\text{OH}$  ice. Although we calculate a number of  $\text{CH}_3\text{OH}$  lattice modes of similar band strength below  $200\ \text{cm}^{-1}$ , they are not particularly resolved or of high intensity in the thin film experiment. For the example of  $\text{CH}_3\text{CHO}$ , its most intense band lies on what is generally considered the limits of the far-IR region, its  $520\ \text{cm}^{-1}$   $\nu_{10}$  CCO deformation fundamental. However,  $\text{CH}_3\text{CHO}$  also features the most intense band structure of our molecules below  $160\ \text{cm}^{-1}$  (the lowest of the  $\text{H}_2\text{O}$  lattice bands). Here,  $\text{CH}_3\text{CHO}$  thin film experiments show a cluster of three narrow resolved peaks at  $74$ ,  $96$  and  $120\ \text{cm}^{-1}$  that could be used to confirm its presence in a mixed ice. Finally, for  $\text{CH}_3\text{COOH}$ , its presence on a mixed water-ice surface could be confirmed by its intense  $A_1$  lattice mode at  $195\ \text{cm}^{-1}$ ; likely to appear as a sharp peak between the water lattice modes. As  $\text{CH}_3\text{COOH}$  displays the best frequency match between thin film experiments and periodic DFT calculation, it is perhaps the best example of our methodology to be adapted to reproduce the convoluted spectra of mixed ice surfaces with separate domains of crystalline material.

On the question if this is the best physicochemical representation of a true TNO surface material is yet to be confirmed, by either observation or experiment. Future experiments will explore the processing of mixed  $\text{H}_2\text{O}/\text{CH}_4/\text{N}_2$  ices by photolysis and particle interactions over planetary time-scales and extrapolate abundance limits for products such as  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$ . Online far-IR analysis of the subsequent warming of these ices will determine at what temperature these phase transitions take place, and perhaps observe the segregation of material into crystalline-phases. The creation of co-crystalline material between polar species could also be a possibility. However, the necessary diffraction data for binary systems of small organics is scarce at this stage, preventing us from performing preliminary calculations on such systems. Low-temperature powder crystallography experiments on prototype co-crystal systems are scheduled for future work at the Australian Synchrotron, to provide the required data for the periodic DFT approach established in this study.

## 5 CONCLUSION

The simulation of far-IR spectra for molecular ices is often inhibited by the high computational cost required to perform periodic boundary calculations on the unit cell of the crystal, often containing upwards of 20 atoms for simple, small molecules of planetary interest. Here, we have utilized the C14 package to greatly reduce both the required resources (to a single processor desktop computer) and calculation time (total  $24\text{--}48\ \text{h}$  for optimization and frequency calculations) by utilizing crystallographic data to reconstruct the periodic molecular system. The required crystallographic data are readily available for crystals of many small, organic species. Using this harmonic approach (at the B3LYP-D3/m-6-311G(d) level) to generate simulated IR spectra, we apply a universal  $0.92$  scaling factor to yield close approximation of the experimental far-IR spectra recorded for the respective crystalline thin film. For the example of  $\alpha\text{-CH}_3\text{OH}$ , some intermolecular lattice modes (such as  $L_{B1}$ ) could be confidently assigned to their far-IR absorption features via predicted frequencies and intensities, while other strong bands appeared in regions too congested to assign. The calculations performed on  $\text{CH}_3\text{CHO}$  did predict the same

number of medium to strong far-IR features to that observed in the experimental spectra; however, the peaks are rather displaced from their calculated positions and are therefore not confidently assigned to specific symmetry species. Finally, the CH<sub>3</sub>COOH simulated spectra provided the most satisfying comparison to experiment after application of the 0.92 scaling factor, with the intense 195 cm<sup>-1</sup> peak well approximated, together with the weak feature at 75 cm<sup>-1</sup>.

This approach is particularly beneficial for the characterization of intermolecular interactions, where molecular displacements can be surveyed using modern analysis software. IR translation and libration modes can be quickly and easily compiled and compared to far-IR data, such as the thin film spectra collected with our setup at the Australian Synchrotron. However, our mid-IR benchmarks suggest that higher level calculations (with or without anharmonic treatment) on small molecular clusters are likely to yield more reliable frequencies for intramolecular/fundamental modes. With pure molecular crystals of simple organics now benchmarked, future investigations will now turn toward co-crystalline materials consisting of multiple molecular carriers as well as mixed-phase ices of planetary relevance, such as those modelled for TNO surfaces. Another possible complementary approach is to employ molecular dynamics to simulate vibrational spectra (Balbuena et al. 2008). As the theoretical and experimental techniques employed in this study mature over time, the process of recreating far-IR spectra to confirm the molecular compositions of distant bodies will hopefully become more accurate and routine.

## ACKNOWLEDGEMENTS

This project has been supported by Australian Research Council via the Discover Early Career Research Award (DE150100301). Auchettl kindly thanks La Trobe University for funding via a PhD scholarship. Theoretical work (Project AY7) was undertaken with the assistance of resources and services from the NCI, which is supported by the Australian Government. We finally thank the reviewers for their thoughtful comments and suggestions for future work.

## REFERENCES

- Albinati A., Rouse K. D., Thomas M. W., 1978, *Acta Crystallographica Section B*, 34, 2184  
 Allodi M. A. et al., 2013, *Space Sci. Rev.*, 180, 101  
 Anderson C. M., Samuelson R. E., 2011, *Icarus*, 212, 762  
 Balbuena P. B. et al., 2008, *J. Phys. Chem. A*, 112, 10210  
 Bennett C. J., Jamieson C. S., Osamura Y., Kaiser R. I., 2005, *Astrophys J*, 624, 1097  
 Bennett C. J., Kaiser R. I., 2007, *Astrophys J*, 660, 1289  
 Civalleri B., Doll K., Zicovich-Wilson C. M., 2007, *J. Phys. Chem. B*, 111, 26  
 Cook J. C., Desch S. J., Roush T. L., Trujillo C. A., Geballe T. R., 2007, *Astrophys J*, 663, 1406  
 Cruikshank D. P. et al., 2015, *Icarus*, 246, 82  
 de Kok R. et al., 2007, *Icarus*, 191, 223  
 Dovesi R., Causa M., Orlando R., Roetti C., Saunders V. R., 1990, *J. Chem. Phys.*, 92, 7402  
 Dovesi R. et al., 2014, *Int. J. Quantum Chem.*, 114, 1287  
 Dumas C., Carry B., Hestroffer D., Merlin F., 2011, *A&A*, 528, 6  
 Ennis C., Auchettl R., Ruzi M., Robertson E. G., 2017, *Phys. Chem. Chem. Phys.*, 19, 2915  
 Flasar F. M. et al., 2004, *Space Sci. Rev.*, 115, 169  
 Gatti C., Saunders V. R., Roetti C., 1994, *J. Chem. Phys.*, 101, 10686  
 Grimme S., 2006, *J. Comput. Chem.*, 27, 1787

- Grundy W. M. et al., 2016, *Science*, 351, 1283  
 Haurie M., Novak A., 1965, *Spectrochim. Acta*, 21, 1217  
 Heyd J., Peralta J. E., Scuseria G. E., Martin R. L., 2005, *J. Chem. Phys.*, 123, 174101  
 Hollenstein H., Gunthard H. H., 1971, *Spectrochim. Acta Part A*, 27, 2027  
 Ibberson R. M., Yamamuro O., Matsuo T., 2000, *J. Mol. Struct.*, 520, 265  
 Ioppolo S., McGuire B. A., Allodi M. A., Blake G. A., 2014, *Faraday Discuss.*, 168, 461  
 Jewitt D. C., Luu J., 2004, *Nature*, 432, 731  
 Kaiser R. I., Maity S., Jones B. M., 2014, *Phys. Chem. Chem. Phys.*, 16, 3399  
 Kirchner M. T., Das D., Boese R., 2008, *Cryst. Growth & Design*, 8, 763  
 McClure M. K. et al., 2015, *Astrophys J*, 799, 13  
 Merlin F., Guilbert A., Dumas C., Barucci M. A., de Bergh C., Vernazza P., 2007, *A&A*, 466, 1185  
 Min M. et al., 2016, *A&A*, 593, 11  
 Moore M. H., Hudson R. L., 1994, *A&AS*, 103, 45  
 Moore M. H., Hudson R. L., 1998, *Icarus*, 135, 518  
 Oberg K. I., 2016, *Chem. Rev.*, 116, 9631  
 Owen T. C. et al., 1993, *Science*, 261, 745  
 Palumbo M. E., Castorina A. C., Strazzulla G., 1999, *A&A*, 342, 551  
 Pascale F., Zicovich-Wilson C. M., Gejo F. L., Civalleri B., Orlando R., Dovesi R., 2004, *J. Comput. Chem.*, 25, 888  
 Pontoppidan K. M. et al., 2008, *Astrophys J*, 678, 1005  
 Schaller E. L., Brown M. E., 2007, *Astrophys J*, 670, L49  
 Shimanouchi T., 1977, *J. Phys. Chem. Ref. Data*, 6, 993  
 Sitko M. L. et al., 2011, *Astron J*, 142, 22  
 Tauer K. J., Lipscomb W. N., 1952, *Acta Crystallogr.*, 5, 606  
 Teanby N. A., Irwin P. G. J., de Kok R., Jolly A., Bezard B., Nixon C. A., Calcutt S. B., 2009, *Icarus*, 202, 620  
 Torrie B. H., Binbrek O. S., Strauss M., Swainson I. P., 2002, *J. Solid State Chem.*, 166, 415  
 Ugliengo P., Viterbo D., Chiari G., 1993, *Z. Kristallogr.*, 207, 9

## SUPPORTING INFORMATION

Supplementary data are available at [MNRAS](https://www.mnras.org) online.

**Figure S1.** Optimized crystal structure for orthorhombic  $\alpha$ -phase CH<sub>3</sub>OH (*P*<sub>2</sub><sub>1</sub>2<sub>1</sub>2<sub>1</sub>) at the B3LYP-D/m-6-311G(d) level. Viewing down a-coordinate (left-hand side) and b-coordinate (above).

**Figure S2.** Optimized crystal structure for orthorhombic  $\beta$ -phase CH<sub>3</sub>OH (*Cmc*<sub>2</sub>) at the B3LYP-D/m-6-311G(d) level. Viewing down c-coordinate (left-hand side) and a-coordinate (above).

**Figure S3.** Optimized crystal structure for monoclinic CH<sub>3</sub>CHO (*P*<sub>2</sub><sub>1</sub>/c) at the B3LYP-D/m-6-311G(d) level. Viewing down a-coordinate (left-hand side) and b-coordinate (above).

**Figure S4.** Optimized crystal structure for orthorhombic CH<sub>3</sub>COOH (*Pna*<sub>2</sub>) at the B3LYP-D/m-6-311G(d) level. Viewing down b-coordinate (left-hand side) and c-coordinate (above).

**Table S1.** CH<sub>3</sub>OH C14 Output File Data: B3LYP-D3/m-6-311G(d) and assignments.

**Table S2.** CH<sub>3</sub>CHO C14 Output File Data: B3LYP-D3/m-6-311G(d) and assignments.

**Table S3.** CH<sub>3</sub>COOH C14 Output File Data: B3LYP-D3/m-6-311G(d) and assignments.

Please note: Oxford University Press is not responsible for the content or functionality of any supporting materials supplied by the authors. Any queries (other than missing material) should be directed to the corresponding author for the paper.

This paper has been typeset from a Microsoft Word file prepared by the author.