Ab-initio density-functional lattice-dynamics studies of ice

A.S. Côté, I. Morrison, X. Cui, S. Jenkins, and D.K. Ross

Abstract: We present the results of first-principles computational studies of the dynamical properties of hexagonal ice using both the ab-initio pseudopotential method and the full-potential augmented plane-wave method. Properties obtained using both the generalized gradient approximation (GGA) and the meta-GGA in density-functional theory are compared. The lattice-dynamical properties of the structures are obtained using a finite-difference evaluation of the dynamical matrix and force-constant matrix from atomic forces. Phonon dispersion is evaluated by the direct determination of the force-constant matrix in supercells derived from the primitive molecule unit cells with the assumption that force constants are zero beyond the second molecular nearest neighbors. The k-dependent phonon frequencies are then obtained from the force-constant matrix and dispersion relations, and the Brillouin-zone integrated density of states is evaluated. The importance of phonon dispersion in the various regions of the phonon spectra is then assessed and compared to existing neutron-scattering data. Frozen-phonon calculations are used to compare phonon frequencies evaluated in both the GGA and meta-GGA.

PACS Nos.: 61.12Ex, 63.20Dj

Résumé : Nous présentons les résultats de calculs fondamentaux des propriétés dynamiques de la glace hexagonale utilisant les deux méthodes du pseudo-potentiel ab initio et de l'onde plane augmentée du potentiel complet. Nous comparons les propriétés obtenues, utilisant d'une part l'approximation du gradient généralisé (GGA) et d'autre part du méta-GGA pour la fonctionnelle de densité. Les propriétés dynamiques en réseau des structures sont déterminées en solutionnant par différences finies les matrices dynamiques et les matrices de constantes de force obtenues des forces atomiques. Nous évaluons la dispersion des phonons en déterminant directement la matrice de constantes de force dans les super-cellules dérivées des cellules moléculaires primitives, dans l'hypothèse où les constantes de force sont nulles au delà du deuxième plus proche voisin. La dépendance en k de la fréquence des phonons est alors obtenue de la matrice de constantes de force et des relations de dispersion et la densité d'états intégrée de la zone de Brillouin est aussi évaluée. L'importance de la dispersion des phonons dans les diverses régions du spectre est alors estimée et comparée aux données existantes en diffusion de neutrons. Nous utilisons des calculs sur phonons gelés pour comparer les fréquences de phonon dans les deux approches, GGA et méta-GGA.

[Traduit par la Rédaction]

Received 15 July 2002. Accepted 16 December 2002. Published on the NRC Research Press Web site at http://cjp.nrc.ca/ on 19 March 2003.

A.S. Côté, I. Morrison,[1] X. Cui, and D.K. Ross. Institute for Materials Research and Joule Physics Laboratory, University of Salford, Salford, M5 4WT, U.K.
S. Jenkins. Department of Informatics and Mathematics, University of Trollhättan/Uddevalla, S-461 29 Trollhättan, Sweden.

[1]Corresponding author (e-mail: i.morrison@salford.ac.uk).

 doi: 10.1139/P03-003

1. Introduction

The lattice-dynamical properties of ice have been probed over a number of decades using spectroscopies that include infrared absorption, Raman spectroscopy, and inelastic neutron scattering [1]. Spectra have been obtained for a wide variety of ambient and high-pressure polymorphs of ice [2]. The spectra obtained contain a wealth of information concerning the nature of the microscopic chemical-bond dynamics but are difficult to interpret because of the complexity of the structures and the corresponding complexity of the dynamics. Modeling plays a key role in spectral interpretation and the linking of features to their microscopic origin. Potential-based empirical modeling has had some success towards this end, but to date, there are no empirical potentials capable of describing ice dynamics and related properties across its whole spectra range and describing certain key spectral features. First-principles methods provide a route to modeling atomistic dynamics without prejudice to bond properties. Probably the most computational tractable first-principles frameworks to this end in periodic crystals are based on semi-local approximations to the density-functional theory (DFT) description of the many electron problem. Previous studies [3] have demonstrated the success of the generalized gradient approximation (GGA) [4] to DFT in describing vibrational density of states (VDOS) across the ice phase diagram. Density of states in these previous studies were obtained by direct determination of Brillouin-zone center frequencies in small supercells, the effects of dispersion being incorporated at a crude level. In this study, we present the first ab-initio determination of k-vector-dependent frequencies and full Brillouin-zone integrated VDOS. The computational methods employed are presented in Sect. 2. VDOS and dispersion relations are presented in Sect. 3 together with a discussion of the key features in the VDOS and dispersion relations, and comparisons are made with neutron data. The importance of electron correlation effects in hydrogen bonds make an accurate DFT-based description of bond dynamics very difficult. For example, as pointed out in Sect. 3, in the GGA to DFT hydrogen-bond frequencies are seriously overestimated. In Sect. 5, we compare frozen-phonon frequencies evaluated in the GGA and recently proposed meta-GGA [5] and comment on its suitability as a method of choice in the first-principles modeling of ice. Brief final conclusions are made in Sect. 5.

2. Computational methods

The dynamical calculations are calculated using the ab-initio pseudopotential method as employed in the CASTEP code [6] using ultrasoft pseudopotentials [7] to model the effect of oxygen-core electrons and provide efficient plane-wave expansions of valence electrons. The GGA [4] is used to describe the exchange correlation interactions. This approach allows plane-wave basis sets with a kinetic energy cutoff of 380 eV to be used. Within this framework, we find typical O–O distances to be predicted to be ~2.5% too small compared to experiment with the majority of this difference being due to the hydrogen bond. This is in contrast to previous studies that employed a harder norm-conserving pseudopotential for oxygen and a bare Coulomb potential for hydrogen [3] where O–O distances were predicted ~2% too small. Here, a plane-wave basis with a 900 eV kinetic-energy cutoff had to be employed to obtain convergence. A recent exacting study by Hamman [8] employing harder, more exacting, pseudopotentials including core corrections and curvilinear co-ordinates to deal with more rapidly varying functions in the core region predict O–O distances within 1% of experiment using the same GGA functional. This suggests that errors in structural parameters in this study are partly due to the pseudopotential approximation and partly due to the GGA. These differences, although larger than typically accepted differences in strongly bonded systems, are still good enough for quantitative studies. The system size needed for this current study is such that it is only made computationally tractable using the ultrasoft pseudopotential method and the resulting reduction in basis size compared to the other approaches above.

The lattice-dynamics method is used to calculate vibrational properties. Previous studies [3] evaluated directly the zone-center dynamical matrix by a finite-difference method based on atomic forces

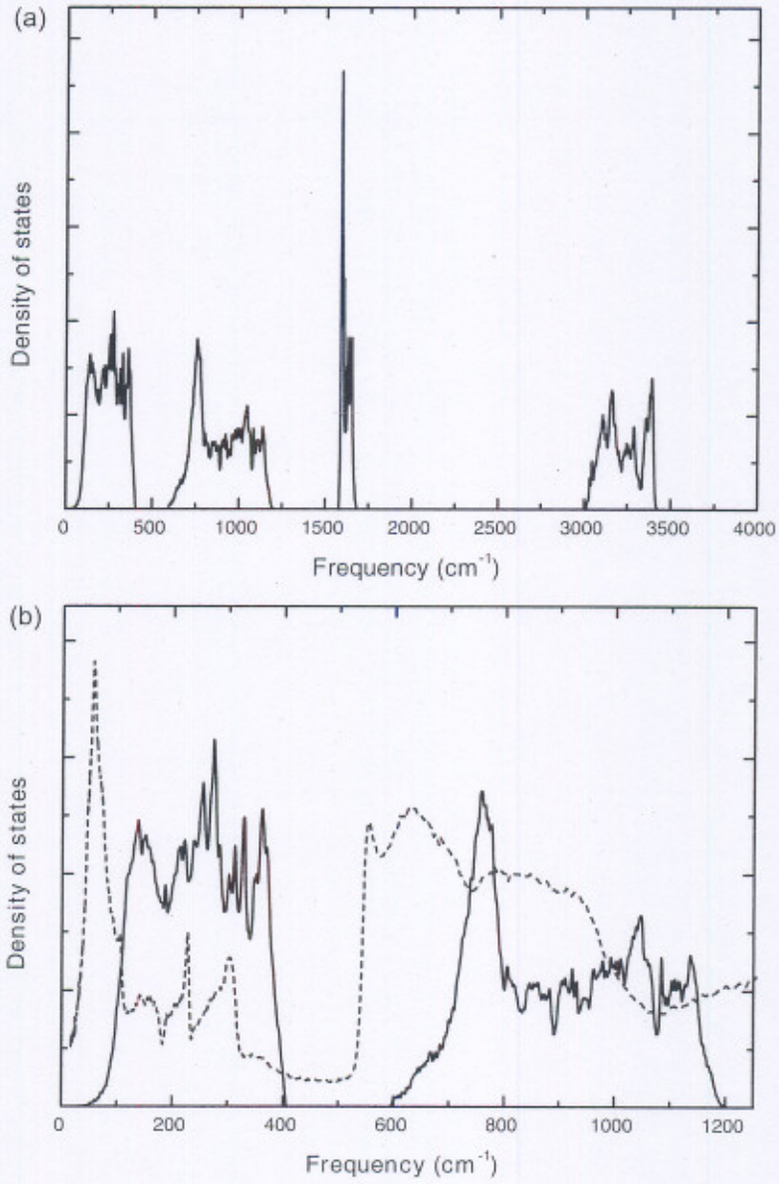
obtained when all atoms in a cell were individually displaced from their equilibrium positions. Here, we extend these studies and directly determine the force-constant matrix in a similar manner with an assumption that force constants are zero beyond second nearest molecular neighbors [9]. Atomic shifts of 0.1 Å are used and both positive and negative shifts employed to cancel anharmonic terms in atomic forces. An eight-molecule primitive cell is employed with calculations of force constants carried out in a $3 \times 2 \times 2$ supercell containing 96 molecules. All internal co-ordinates were relaxed until all atomic forces were less than 10^{-3} eV/Å. Plane-wave basis sets with a kinetic-energy cutoff of 380 eV are employed. Results presented are actually for the structure with $cmc2_1$ symmetry, however, the unit-cell parameters were constrained to be hexagonal with the experimental c/a ratio. The reasoning behind this constraint is that this study is part of a larger one modeling the VDOS in disordered ice Ih, to this end a number of eight-molecule supercells containing differing molecular orientations are being used and employing the same primitive cell for each structure is important. The cell volume chosen is the average of the minimized volumes over these structures. Once the force-constant matrix has been determined, the k-dependent dynamical matrices using the standard lattice-dynamics approach [10] are subsequently diagonalized to obtain frequencies and normal-mode eigenvectors. This is done for both hydrogenated and deuterated structures. It should be pointed out that this method does not incorporate the effects of TO–LO (transverse optic – longitudinal optic) splitting in the zone-center frequencies, however, empirical estimates of this splitting in this molecular dipolar structure [11] show it to be of the order 10 meV and will not significantly effect the results presented here. In principle, linear response theory could be employed to obtain the Born effective changes from which the TO–LO can be directly calculated but at a much greater computational cost. The VDOS presented in Sect. 3 are integrated over the Brillouin zone by evaluating frequencies on a fine grid and summing over a set of broadened Gaussians with 1 cm^{-1} half-width half-maximum, the grid was refined until no changes in the VDOS were observed.

3. Results and discussion

The VDOS for both hydrogenated and deuterated ice are presented in Figs. 1*a* and 2*a*, respectively. We clearly see bands of frequencies corresponding to the molecular translation modes (0–400 cm^{-1} H_2O, 0–380 cm^{-1} D_2O); molecular librational modes (600–1200 cm^{-1} H_2O, 420–850 cm^{-1} D_2O); intra-molecular bending modes (1580–1680 cm^{-1} H_2O, 1150–1220 cm^{-1} D_2O); and covalent-bond stretching modes (3010–3430 cm^{-1} H_2O, 2190–2510 cm^{-1} D_2O). An enlargement of the intermolecular frequency range in each case is also presented in Figs. 1*b* and 2*b*. We also superimpose the inelastic neutron-scattering spectra [12] on Fig. 1*b* for comparison. The comparison is made with the ice Ih data as data for the $cmc2_1$ structure, ice XI, was unavailable. In the translational region there is very little difference between the neutron data for ice Ih and ice XI, in the rotational region there are some differences [2], which better agree with the calculated spectra. In general, the H_2O and D_2O spectra are very similar with the deuterated frequencies being brought down slightly in the translational and rotational regions and significantly in the bending and stretching regions. The finer structure in each band of the H_2O and D_2O spectra are essentially the same. An obvious difference in the neutron spectra and calculated spectra is the position of the upper edge in the translational optic region, the calculated value is some 80 cm^{-1} too high, this discrepancy is discussed further in Sect. 4. That apart, the general agreement of features in the translational optic region is good with two distinct peaks present at 400 and 270 cm^{-1}, there are also finer splittings present in the calculated spectra not present in the neutron data possibly due to the ordered structure modeled here. The origin of this splitting is coupling with covalent-bond stretching modes as briefly discussed elsewhere [13], a more detailed account will appear shortly. We see a similar splitting in the covalent-bond stretching region. Here, the upper frequency peak corresponds to a symmetric stretching motion with adjacent molecules in antiphase and the low-frequency peak to symmetric stretching in-phase motion.

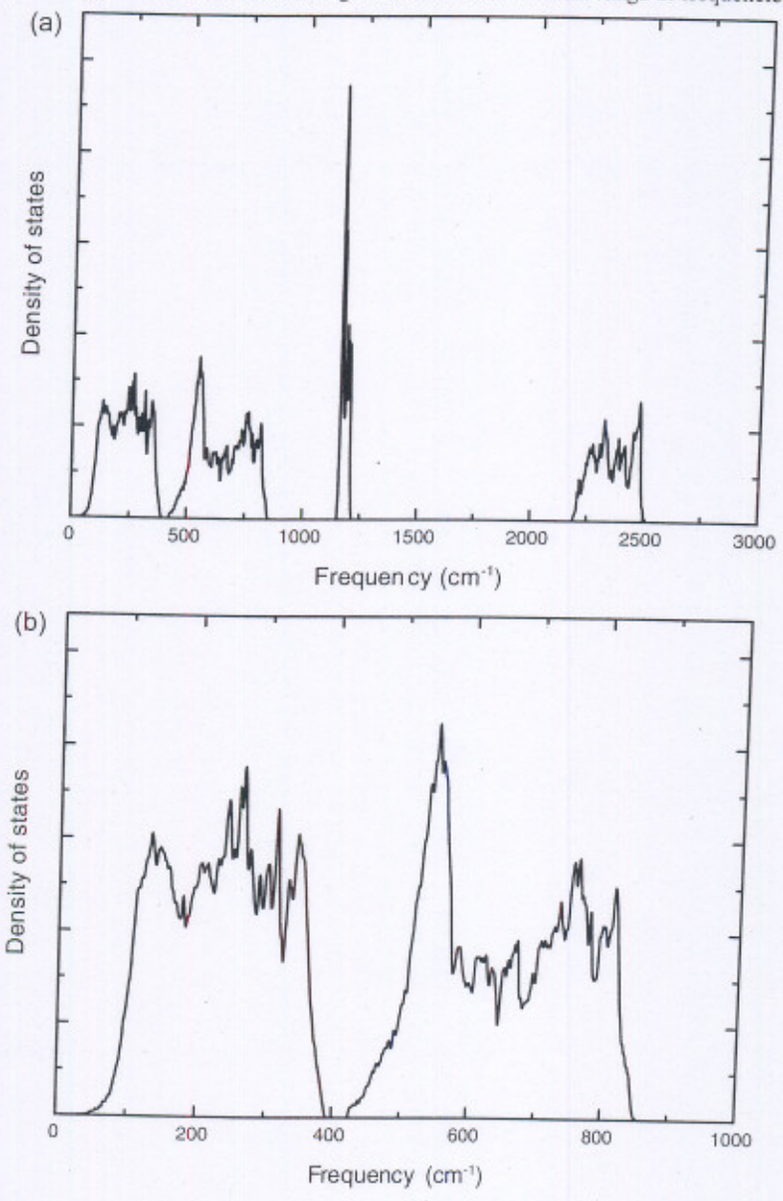
Finally, we present dispersion relations for H_2O ice in the translational and covalent-bond stretching

Fig. 1. (*a*) The total vibrational density of states across the whole frequency range for the hydrogenated structure. The figure was obtained by summing over Gaussian-broadened frequencies on a fine grid in k-space as explained in the text. (*b*) A enlargement of the VDOS in Fig. 1*a* in the intermolecular range of frequencies. The broken line is the inelastic neutron scattering data available from ref. 12.



regions in Figs. 3 and 4. Dispersion relations are presented in the Brillouin zone of the eight-molecule orthorhombic cell along the three Cartesian directions. To compare this directly to dispersion in the higher symmetry hexagonal structure bands need to be folded out. For example, the dispersion relation in x corresponds to a folded dispersion from Γ to K in the hexagonal zone. Note that force constants have not yet been adjusted to satisfy the sum rules [9], hence, low-frequency acoustic modes are not well reproduced. Examination of the dispersion relations reveals several flat bands that result in the features discussed above. Also, in the translational optic region, we see a single folded band connecting

Fig. 2. (*a*) The total vibrational density of states across the whole frequency range for the deuterated structure. The figure was obtained by summing over Gaussian-broadened frequencies on a fine grid in k-space as explained in the text. (*b*) A enlargement of the VDOS in Fig. 2*a* in the intermolecular range of frequencies.



these regions of flat bands. There is some very limited evidence of this band in the neutron dispersion relation [2,14].

4. Comparison of density functionals

The calculations presented above show that hydrogen-bond frequencies calculated within the GGA are typically too high. For example, the upper edge of the molecular translational optical region of the spectra are ~400 cm^{-1} compared to a value of ~320 cm^{-1} as measured in neutron experiments (see Fig. 1*b*). This discrepancy makes truly quantitative interpretation of spectral features difficult in

Fig. 3. Dispersion relations in the translational frequency range for the hydrogenated structure. Dispersion is plotted along the Cartesian directions from zone center to zone edge in the Brillouin zone of the orthorhombic eight-molecule unit cell.

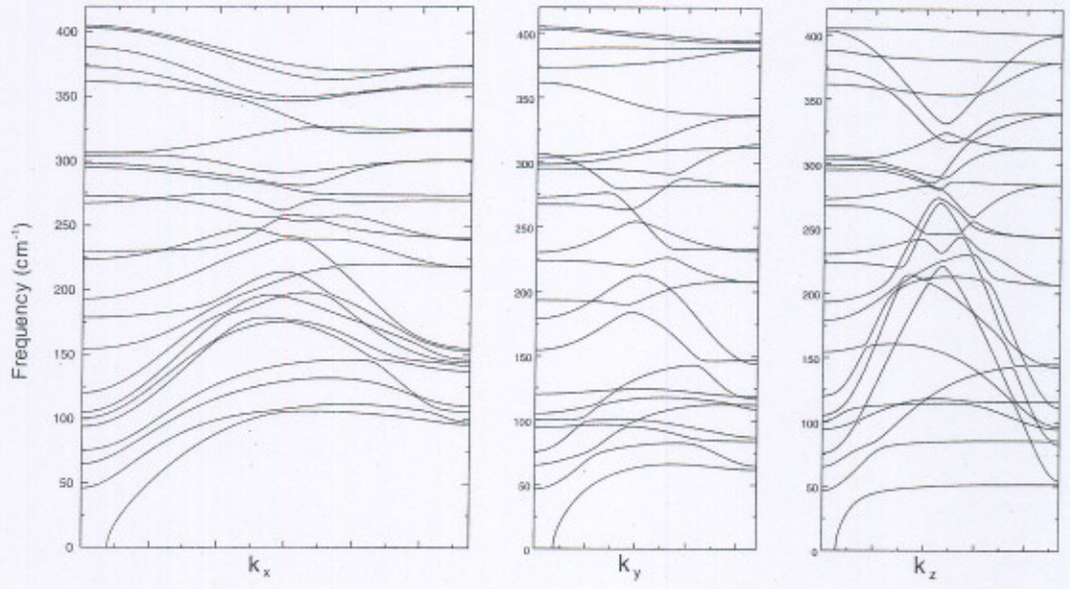
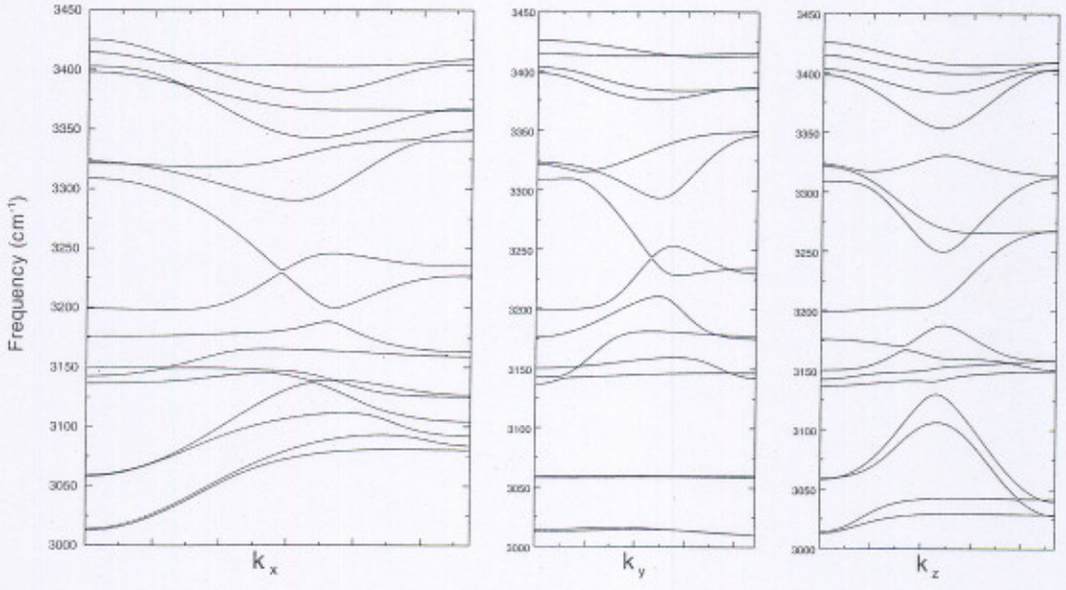


Fig. 4. Dispersion relations in the molecular stretch frequency range for the hydrogenated structure. Dispersion is plotted along the Cartesian directions from zone center to zone edge in the Brillouin zone of the orthorhombic eight-molecule unit cell.



some regions. The source of this error is the sensitivity of the hydrogen bonds to electron correlation effects, improvement in predicted hydrogen-bond frequencies demands a description of exchange-correlation functionals beyond the GGA. Here, we investigate whether the recently proposed meta-GGA functional [5] offers significant improvement of this property. The meta-GGA functional is a truly ab-initio functional that depends on the density of charge, ρ, the gradient of charge, $\nabla\rho$, and second

derivatives of ρ through the noninteracting kinetic-energy density $\tau = \frac{1}{2}\sum_{i}^{occ}(\nabla\phi_i)^2$. Importantly, the meta-GGA functional is a semi-local functional and results in a local exchange correlation potential. This means the meta-GGA is more computationally efficient than hybrid schemes [15,16] that use a mixture of exact exchange and the GGA to improve the description of many electron effects. It has been pointed out that hybird schemes give better hydrogen-bond disassociation energies [16] in small molecular clusters but the computational cost associated with the nonlocal exact exchange operator mean they are not the method of choice in extended systems.

We have performed frozen-phonon calculations using the APW plus local orbital methods as implemented in the WIEN2K [17] code to compare hydrogen-bond frequencies in the GGA and meta-GGA. The method is an all-electron method, hence, any errors due to the pseudopotential approximation are completely removed. Atomic spheres of radii 0.6 bohr for hydrogen and 1.2 bohr for oxygen were used together with an RK parameter of 5. The computational cost of this method is considerably higher than the pseudopotential method, hence, only frozen-phonon calculations are feasible to evaluate frequencies. The phonon mapped was a zone-center LO phonon along the c-axis of the $cmc2_1$. The energy surface obtained when rigid molecules hydrogen bonded in the z direction were moved towards and away from each other. The curvature around the equilibrium position was found by fitting to a fourth-order polynomial and corresponding frequencies evaluated in each case. We calculate the frequency in the GGA to be 390 cm^{-1} and that in the meta-GGA to be 361 cm^{-1}. Thus, we see the meta-GGA does offer some improvement in the hydrogen-bond frequencies but does not completely resolve the difference as compared to experiment. We also note that molecular rotational relaxation was not taken into account when mapping the phonon energy surface, its inclusion must reduce the predicted frequency further towards the experimental one. We also note that frequencies calculated in the GGA are lower here than in the previous section employing the pseudopotential method implying some of the error in frequencies is due to the pseudopotential method.

5. Conclusions

We have performed the first complete ab-initio determination of k-dependent vibrational frequencies and related spectra and dispersion relations. The calculations demonstrate the ability of state-of-the-art methods in first-principles simulation coupled to high-performance computing to directly simulate the dynamical properties of a system as complex as ice. Although quantitative agreement with experiment is not achieved, the agreement is such that some information relating to the microscopic origin of spectral features can still be obtained. We also show that the meta-GGA is expected to offer some improvement in the evaluated frequencies but not enough for qualitative agreement. Our results show that there is still a need for improvements in the calculational methodologies before quantitative agreement is obtained. Possible routes to improvement include the use of nonlocal energy functionals and the evaluation of Born effective charges, and work is in progess towards this end.

Acknowledgements

We thank the ORS (U.K.) and the University of Salford for the financial support of X.C. during this work. All calculations in this study were performed on facilities in the Center for High Performance Computing at the University of Salford funded by the HEFCE and IBM (U.K.) through the JREI scheme.

References

1. V.F. Petrenkov and R.W. Whitworth. Physics of ice. Oxford University Press, Oxford. 1999.
2. J. Li. J. Chem. Phys. **105**, 6733 (1996) and references therein.
3. S. Jenkins and I. Morrison. J. Phys. Condens. Matter, **13**, 9207 (2001) and references therein.
4. J.P. Perdew, K. Burke, and M. Ernzerhof. Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997).

5. J.P. Perdew, S. Kurth, A. Zupan, and P. Blaha. Phys. Rev. Lett. **82**, 2544 (1999).
6. M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos. Rev. Mod. Phys. **64**, 1045 (1993).
7. D. Vanderbilt. Phys. Rev. B: Condens. Matter, **41**, 7892 (1990).
8. D.R. Hamman. Phys. Rev. B: Condens. Matter, **55**, 10157 (1997).
9. G.J. Ackland, M.C. Warren, and S.J. Clark. J. Phys. Condens. Matter, **9**, 7861 (1997).
10. M. Born and K. Huang. Dynamical theory of crystal lattices. Oxford University Press, Oxford. 1956.
11. D.D. Klug, J.S. Tse, and E. Whalley. J. Chem. Phys. **95**, 7011 (1991).
12. Data is taken from the ISIS INS database on the web at http://www.isis.rl.ac.uk/molecularspectroscopy.
13. I. Morrison and S. Jenkins. Phys. B: Phys. Condens. Matter, **263**, 442 (1999).
14. B. Renker. *In* Physics and chemistry of ice. *Edited by* E.Walley, S.J. Jones, and L.W. Gold. University of Toronto Press, Toronto. 1973. p. 82.
15. C. Adamo, M. Ernzerhof, and G.E. Scuseria. J. Chem. Phys. **112**, 2643 (2000).
16. A.D. Rabuck and G.E. Scuseria. Theor. Chem. Acc. **104**, 439 (2000).
17. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz. WIEN2k: An augmented plane wave and local orbitals program for calculating crystal properties. Karlheinz Schwarz, Techn. Universität Wien, Austria. 2001. ISBN 3-9501031-1-2.