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DFT and Local-MP2 Periodic Study of the Structure and Stability of Two Proton-Ordered Polymorphs of Ice

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The equilibrium geometry and the formation energy of two periodic polymorphs of Ice have been theoretically studied: the former (Ice XI, crystal group $Cmc2_1$) is experimentally observed as the most stable structure at low temperature and pressure; the latter (crystal group $Pna2_1$) is the simplest proton-ordered model of ordinary ice. With the Crystal code, the problem is solved using Hartree–Fock (HF), pure Kohn–Sham (PW91), or hybrid (B3LYP) one-electron Hamiltonians. The B3LYP results are those in best agreement with the experiment. Using the B3LYP-optimized geometry and starting from the corresponding HF Crystal solution, the energetics of the two polymorphs have been investigated at an ab initio MP2 level using the Cryscor code, based on a local-correlation approach: these calculations have allowed us not only to confirm the excellent B3LYP results as concerns the formation energy and the relative stability of the two structures but also to analyze the role in this respect of the intra- and intermolecular contributions to the correlation energy. Since both Crystal and Cryscor adopt a basis set of localized Gaussian-type functions and since very small energy differences are involved, utter attention has been paid to correcting for the basis set superposition error in the calculation of formation energies.

I. Introduction

Ice XI is the only proton-ordered phase of ordinary ice at low pressure. The transition of KOH-doped ice samples at 72 K to this phase, reported more than two decades ago,^{1,2} has allowed some fundamental questions of ice physics to be answered: in particular, the residual entropy of ordinary ice (Ih) at 0 K, already known since 1933³ and modeled by Pauling in 1935,⁴ was finally understood in terms of kinetic constraints in the reorientation process of water molecules within the crystal. The role of alkali hydroxides (in particular of potassium hydroxide) has been studied both experimentally through dielectric and calorimetric studies^{1,5} and theoretically^{6,7} by means of an embedded cluster method: they might act as catalysts for the reorientation process by creating protonic point defects within the crystal which locally violate the short-range order imposed by the two *ice rules* (two hydrogens adjacent to each oxygen and one hydrogen per O---O bond).⁸

The structural properties of Ice XI have been successfully studied through neutron diffraction experiments carried out on KOD-doped D₂O ice.⁹ The space group was found to be the orthorhombic $Cmc2_1$ one, with four water molecules per cell and a net dipole along the *c* axis. This first experiment, however, was performed on a sample characterized by a small degree of transformation; new measurements performed at 5 K in 1996¹⁰ are here taken as the experimental structural reference. The ferroelectric character of Ice XI has been confirmed by thermally stimulated depolarization experiments.¹¹ From a theoretical point of view, however, the reason for the special stability of this ferroelectric structure with respect to other proton-ordered ice polymorphs is still obscure. Howe first showed that 17 orthorhombic symmetry-independent structures of ordinary ice (Ih) with four or eight molecules per unit cell can be considered.¹² Among these, the one originally proposed by Bjerrum as the most stable

structure,¹³ and later reconsidered by Davidson and Morokuma¹⁴ as a simple model of ordinary ice, has been given special attention: it is an antiferroelectric structure with space group $Pna2_1$, hereafter named P-Ice; Ice XI and P-Ice are schematically shown in Figure 1. A number of studies adopting different kinds of interatomic model potentials have been applied to the problem of the relative stability of the different ice polymorphs (two recent ones by Rick can be cited^{15,16} which also contain ample reference to previous work); however, the results are critically dependent on the potential adopted and in most cases predict the wrong stability order. An ab initio quantum mechanical approach appears therefore mandatory. Periodic calculations performed at the Hartree–Fock (HF) level^{6,7} found Ice XI and P-Ice to be practically isoenergetic, so suggesting the importance of electron correlation effects in determining the extra stability of Ice XI. Hirsch and Ojamäe¹⁷ have recently reconsidered the problem by studying the relative stability of the 16 energy-independent Howe’s polymorphs (two of them are enantiomorphs to each other): we will refer below to this important work as HO. They performed for this purpose very accurate periodic density functional theory (DFT) calculations in a generalized gradient approximation (GGA) using two different codes, Castep¹⁸ and DMol3.^{19,20} With the former program, the PW91²¹ functional together with ultrasoft pseudopotentials and a plane-wave (PW) basis set were used; all geometries were fully optimized. With the latter, the BLYP^{22,23} functional and an atom-centered numerical basis set (split-valence plus polarization functions) were used; only internal coordinates were optimized in this case. The order of stabilities of the 16 structures was the same with the two methods, the $Cmc2_1$ phase resulting the lowest in energy. In particular, the energy difference between Ice XI and P-Ice was found to be -0.10 kcal/mol at the PW91 level and -0.15 kcal/mol at the BLYP level, which is in reasonable agreement

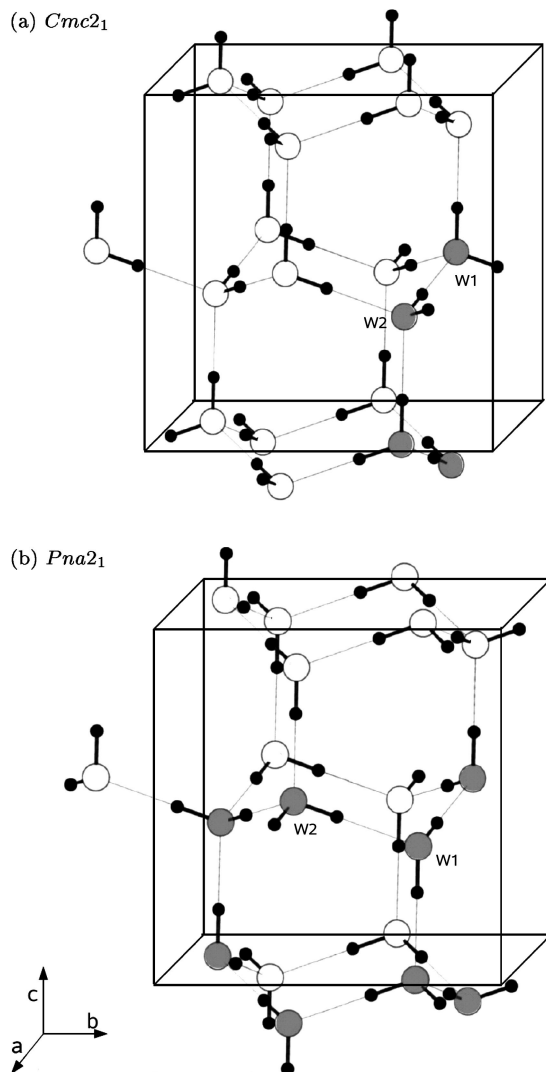


Figure 1. Ice XI (a) and P-Ice (b) structure; the oxygens of the molecules in the unit cell are shaded. In the following, we shall denote as W1 the water molecules with one OH bond along the *c* axis, W2 the others.

with the difference in stability between Ice XI and Ice Ih estimated by Johari²⁴ through extrapolation of experimental data to a hypothetical full degree of transformation (-0.06 kcal/mol). This important result is not conclusive, because local-exchange-correlation DFT is unable to describe *long-range* dispersive interactions and since it is known to overestimate the importance of intermolecular O–H with respect to intramolecular OH bonds. As a matter of fact, the calculated formation energy of Ice XI from gas-phase molecules (E_f) reported in HO is appreciably larger than the experiment, and the difference between the calculated equilibrium geometry and the experimental one is non-negligible. On the other hand, the fact that DFT, at variance with HF, seems to provide unambiguously the correct stability order might indicate that only short-range correlation effects which are accurately described in that approximation are important in this respect. However, the HO results were not entirely coincident with those of a periodic study²⁵ performed by us independently and about at the same time as theirs, using various Hamiltonians (HF, DFT-PW91, and hybrid-exchange B3LYP²⁶) and two different codes (Crystal²⁷ and Vasp²⁸). As concerns in particular PW91, while the Crystal calculations performed with local basis functions confirmed Ice XI

to be more stable than P-Ice (by -0.15 kcal/mol), the Vasp ones, adopting a computational setup practically identical with that of Castep in HO, surprisingly provided the opposite indication, with a stability difference of 0.06 kcal/mol. We shall come back to these contradictory results in the following.

We consider once again in this paper the problem of the special stability of Ice XI. The main motivation for doing so is that we can now use for this purpose a fully periodic ab initio post-HF approach, as implemented in the Cryscor code,²⁹ which could shed new light on the role of electron correlation effects. The main features of Cryscor are recalled in subsection IIC. Essentially, it adopts a local-correlation scheme³⁰ suitably modified for crystals^{31–34} for computing energy and wave function in the lowest post-HF order of perturbation, namely second-order Møller–Plesset theory (MP2). The HF reference solution is provided by the well-known Crystal code in its latest version (Crystal06).³⁵ In spite of its crude account of correlation effects, this local-MP2 (LMP2) approach represents a unique combination of attractive features for the present application: (i) it is completely ab initio; that is, it does not contain empirical parameters; (ii) it takes full account of translational periodicity; (iii) it describes *exactly* long-range dispersive interactions; (iv) MP2 is known to perform satisfactorily with hydrogen-bonded systems.³⁶ The two codes are used here for studying the structure and energetics of Ice XI; a systematic comparison is performed with P-ice, taken as a prototype model of Ice Ih. The role of Crystal in the present investigation is not limited to providing the HF reference solution for Cryscor. In fact, the HF+LMP2 approach is accompanied by an accurate DFT treatment of the same problem performed with Crystal using both a GGA functional, PW91, and a hybrid-exchange one, B3LYP.²⁶ There are several reasons for this choice:

1. Both programs use a local basis set (BS) of contracted Gaussian type Functions (GTF); the choice and calibration of such BSs is known to be a crucial issue. The reproduction of the PW91 results obtained by HO with a practically complete BS of PWs¹⁷ could be a useful guideline for this purpose.

2. The puzzling differences mentioned above between the HO results and our previous ones²⁵ may be indicative of the fact that computational inaccuracies have been underestimated in either study which can become essential when comparing very similar total energies. We can now reconsider this problem taking advantage of the fact that the present Crystal version³⁵ permits much more accurate calculations to be performed with respect to the one used in our preceding paper,²⁷ especially as concerns geometry optimizations.

3. It is interesting to verify the performance of the hybrid B3LYP functional in comparison with the pure GGA ones (PW91, BLYP) employed by HO:¹⁷ it is shown below that also in this case, as in previous studies concerning hydrogen-bonded systems,^{37,38} the B3LYP results are excellent, as concerns both equilibrium geometry and energetics.

4. At variance with Crystal, the Cryscor code does not yet allow the analytical calculation of energy gradients. Hence, the full HF+LMP2 geometry optimization is practically unfeasible. Since the optimized HF geometry is very far from the experiment, the Cryscor calculations have been performed with reference to the optimized B3LYP geometry. This assumption is justified below (section IIIB).

5. The Crystal code provides a useful tool also for the study of vibrational frequencies. This is very interesting in the present case, since Ice XI presents a peculiar spectrum with respect to ordinary ice, especially in the librational region.³⁹ Again, the

B3LYP normal modes can be taken as a reference for ascertaining the role of electron correlation effects on the frequencies; this topic is addressed in a parallel paper.⁴⁰

While the present paper was ready to be submitted, a preliminary report appeared about a post-HF study of ordinary ice by Hermann and Schwerdtfeger.⁴¹ For some aspects their approach is similar to ours: the same periodic code (Crystal06) has been used for generating the reference HF solution, and the BS adopted is also close to ours. However, for evaluating the correlation correction (at an MP2 and coupled-cluster level of approximation), an *incremental* scheme has been adopted,⁴² which considers correlation effects in molecular clusters of increasing size using a molecular code. The incremental technique allows higher levels of theory to be used but does not allow a detailed comparison between quasi-equivalent structures. In fact, the aim of those authors was rather that of investigating the importance and range of correlation corrections in ice, and of assessing the adequacy of the techniques adopted. We shall make a brief reference to their results in our conclusions.

This paper is organized as follows:

Section II revises summarily some critical aspects of the computational setup and in particular: the choice of the GTF BS (section IIA); the setting of the Crystal computations (section IIB); the choice of the main input parameters in Cryscor, in the frame of a brief review of the scheme there used (section IIC); the technique adopted for estimating the basis set superposition error (BSSE)⁴³ (section IID). Further details are provided in ref 44.

In section III our results are reported, first those obtained with Crystal using one-electron Hamiltonians (section IIIA), and next those resulting from the HF+LMP2 calculations with Cryscor (section IIIB); they are critically discussed with reference to experimental data and to the results of previous simulations.

Some general conclusions are drawn in section IV.

II. Computational Setup

A. Basis Set Calibration. Two BSs of contracted GTFs (conventionally named atomic orbitals, AO) have been tried.⁴⁴ The former (hereafter called BSA), of type 6-311G(d,p), is the same as in our previous study of Ice;²⁵ the latter (BSB), of type TZP, that is, of quality triple- ζ plus polarization functions, has been set up after accurate calibration for the DFT study of crystalline urea.³⁷ They differ qualitatively in two respects. BSA adopts Pople's constraint of equal s and p exponents, while BSB treats s and p shells independently so allowing larger variational freedom; second, the external AOs are significantly more diffuse in BSB. All geometry optimizations here have been performed with Crystal using both BSs and have provided quite similar results as concerns geometries, while some differences are observed in calculated energies. It is shown in section IIIA that our PW91 results obtained with BSB are very similar to those reported by HO for the same structures and the same Hamiltonian, but using a PW BS. This result can be taken as indicative that our BSB is close to completeness as regards the definition of the Slater determinant which describes the ground-state wave function in HF and Kohn–Sham-type DFT calculations.

The case is different for the MP2 calculations. As it is recalled in section IIC, the employed BS here should be able to reproduce accurately also the energy distribution and the angular and radial features of the low-lying *excited* one-electron states. Two problems must be mentioned for this purpose which limit the range of BSs usable in Crystal (and therefore in Cryscor). First, the highest GTF angular moment presently manageable by

Crystal is 3 (f functions). Second, the use of very diffuse GTFs may lead to redundancies and numerical instabilities in periodic systems, so preventing convergence of the HF or DFT self-consistent procedure. Here, BSA and BSB have been used also for the MP2 calculations. The possible effect of BS limitations on the corresponding results is discussed below.

B. Computational Parameters in Crystal. Very tight tolerances have been adopted for the Crystal computations, both as concerns the evaluation of single-point energies and the determination of equilibrium geometries, as specified in detail in ref 44. In particular, the new capabilities of Crystal06 allow us to use a finer integration grid and a denser sampling of reciprocal space along with a more stringent set of thresholds for the optimization process, with respect to those used in our previous study.²⁵ Some of the BSA results there reported are directly comparable to the present ones: while the general picture is confirmed (for instance, as regards the effect of the various Hamiltonians), there are small but significant differences concerning equilibrium geometries and formation energies. These inconsistencies, however, can be understood precisely in terms of the computational setups employed: for instance, by performing a single-point BSA-PW91 level calculation using the optimized structure of Ice XI reported by Casassa et al. but with the present computational setup, an energy difference of 0.220 kcal/mol was found with respect to the present minimum, which is quite large when dealing with relative stabilities of ~ 0.1 kcal/mol, with which we are concerned here. Similar computational inaccuracies may be responsible for the disagreement of the Vasp results reported there with respect to the Castep ones by HO, which were obtained using extremely tight criteria.⁴⁵ For this reason, we will not discuss the data in ref 25 any longer.

C. Cryscor and the Setting of Its Main Parameters. We refer to previous papers for a detailed description of theory, algorithms, computational scheme, and capabilities of Cryscor;^{31–34} here we recall its main features, in order to fix the nomenclature, to introduce the settings adopted, and to prepare the discussion of the results.

To represent the occupied HF manifold Cryscor uses Wannier functions (WF) generated by Crystal:⁴⁶ they are well-localized, symmetry-adapted, mutually orthogonal, translationally equivalent functions. In the present application, we consider only correlation between valence electrons; there are therefore four WFs per water molecule, each containing two electrons: two bond and two lone-pair ones. The virtual HF manifold is described instead by the nonorthogonal set of the “projected atomic orbitals” (PAO); they are obtained in Cryscor from the individual AOs of the BS, by projecting out their components in the occupied subspace. WFs and PAOs are labeled with Latin letters: i, j, \dots and a, b, \dots , respectively; they play an essential role in Cryscor, and most computational parameters are related to their definition and use.

The MP2 energy $E^{(2)}$ can be written as a sum of “pair energies” $E_{ij}^{(2)}$, each corresponding to all 2-electron excitations from the ij pair of WFs to two PAOs in the virtual manifold; translational symmetry allows us to impose the first WF (i) to belong to the reference zero cell. The local-correlation Ansatz³⁰ permits all excitations except those involving close-by WF and PAO pairs to be ignored, thus leading to an $\mathbf{O}(N)$ scaling scheme. The following selection criteria are adopted. To the general WF (i) a *domain* \mathbf{D}_i is associated; here \mathbf{D}_i is taken to correspond to the whole molecule to which i belongs. Only those excitations are retained in $E_{ij}^{(2)}$ for which (i) both PAOs belong to either \mathbf{D}_i or \mathbf{D}_j and (ii) the distance d_{ij}

between the centers of the two WFs is within a certain value D , here set to 13 Å. The long-range contributions from pairs (ij) beyond D is calculated in Cryscor by using the London αr^{-6} law, with α coefficients obtained from the knowledge of pair interaction energies within D .

Once the relevant WF-PAO bipairs are selected, the main computational task is the evaluation of the 2-electron repulsion integrals (ERI), ($ialjb$), between the respective product distributions. The problem here is that each WF (PAO) is expressed as a linear combination of AOs, in principle up to infinite distance. A tail-truncation parameter t (here set to 0.0001) allows us to truncate these sums by setting to zero the coefficients whose absolute value is less than t . For reasonable values of t , the evaluation of ERIs owing to a 4-index transformation of the analytic integrals between AOs is still a formidable task. A way out of this difficulty is to use instead a periodic variant of molecular density-fitting techniques,^{47–49} with extraordinary savings in computer times and negligible loss of accuracy. Furthermore, if the two WFs are beyond a certain distance D' , here set to 6 Å, the ERI's are evaluated at near zero cost via a multipolar technique.

D. Evaluation of the Basis Set Superposition Error. In calculating the formation energy E^f of the crystal from gas-phase water molecules, account must be taken of the so-called basis set superposition error (BSSE).^{43,50} Among the many proposals, the simplest and for many aspects the most reliable prescription for estimating the BSSE is the full counterpoise procedure (CP) which essentially consists in calculating the reference energy of the isolated molecule by “dressing” it with ghost functions, corresponding in type and position to those it will find on neighboring atoms in the crystalline structure. In both Ice XI and P-Ice there are two types of molecules which differ geometrically from each other and from the isolated molecule in its equilibrium configuration. Therefore, our CP corrected formation energy per molecule may be expressed by the following formula:³⁷

$$E^f = \frac{E_{\text{cry}}}{n} - E_{\text{W}}^{\text{bare}} - \left[\frac{1}{2} (E_{\text{W1}}^{\text{dress}} - E_{\text{W1}}^{\text{bare}} + E_{\text{W2}}^{\text{dress}} - E_{\text{W2}}^{\text{bare}}) \right] \quad (1)$$

Here, E_{cry} is the crystal energy per cell and n the number of water molecules per cell; W, W1, and W2 label a water molecule in its gas-phase equilibrium geometry and the two molecules in the conformation they assume in the crystal optimized geometry, respectively; the label “bare” means that the energy calculation is performed using only the AOs on the three atoms and “dress” that this BS is complemented with all the AOs on atoms of nearby molecules in the crystal within a certain radius r (here set to 5 Å). The quantity in square brackets is our CP estimate of the BSSE.

While this procedure is here always used for the one-electron Hamiltonians, a much simpler recipe (partition method, PM) has been recently proposed for obtaining an estimate of the MP2 contribution to E^f , directly from the calculation for the crystal, which is largely BSSE-free.⁵¹ It is formulated in the frame of local-correlation approaches and consists in excluding from the evaluation of the LMP2 energy those (ij) WF pairs which belong to the same reactant (in the present case, to the same water molecule). It corresponds to assuming that the intramolecular correlation energy is approximately constant for the different geometries considered. The use of PM or of eq 1 for the estimate of the MP2 formation energy of Ice are critically compared below.

TABLE 1: Equilibrium Geometry, Energy Difference with Respect to P-Ice (ΔE), and Formation Energy from Gas-Phase Molecules (E^f) Computed for Ice XI with Different Hamiltonians and BSs^a

Hamiltonian BS	PW91			B3LYP BSB	HF BSB	expt
	BSA	BSB	PW			
V	232.2	241.4	240.4	257.9	298.9	255.8
a	4.377	4.364	4.380	4.437	4.586	4.465
b	7.415	7.694	7.617	7.922	8.478	7.858
c	7.154	7.189	7.207	7.338	7.687	7.292
$\angle\text{HOH}$	107.3	106.4	108.2	106.7	106.8	107.0
d_{OH}	1.007	1.005	0.992	0.987	0.953	0.980
$d_{\text{O-H}}$	1.656	1.692	1.700	1.771	1.947	1.800
$d_{\text{O-O}}$	2.663	2.697	2.692	2.758	2.900	2.780
ΔE	0.12	-0.04	-0.10	-0.06	-0.02	-0.06
E^f	-17.60	-16.77	-16.40	-13.98	-10.44	-14.16

^a The PW data are from ref 17. Distances and angles (angstroms and degrees) are an average on all occurrences in the unit cell; energy data are in kcal/mol. The experimental data are from ref 10 for geometries; from ref 24 for the relative stability of Ice XI with respect to ordinary ice Ih (of which P-Ice is our model); from ref 52 for the formation energy of ordinary Ice from gas-phase molecules (corrected for zero-point energy), to which ΔE is added.

III. Results and Discussion

A. One-Electron Hamiltonians. Some equilibrium geometrical parameters and energy data obtained with DFT and HF techniques for Ice XI are reported in Table 1 and compared to the experimental data. More details (including the equilibrium configuration of P-Ice) are provided in ref 44. The geometrical PW91 results in the first three columns can first be commented on with reference to the experimental data reported in the last column. For all BSs, as expected, the calculated intramolecular OH bond is too long (by about 2%), and the hydrogen bond O-H too short (by about 7%), with respect to the experiment. The latter error is more influential on the overall geometry of the crystal, and the volume is underestimated by almost 9%; the b axis is the most affected by this contraction (by about 4%); this structural anisotropy is probably due to the fact that, as shown in Figure 1a, b is the lattice direction along which the majority of the hydrogen bonds is oriented. On closer inspection, small differences are found between the structural determinations with the three BSs, the BSB geometry being more similar to the PW than to the BSA one. Quite the opposite type of errors (and even larger) with respect to the experiment is observed in the HF determinations of d_{OH} (-3%) and $d_{\text{O-H}}$ (+8%). As a consequence, the volume is overestimated by about 15%; again, the b axis is the most affected by this expansion (+8%). The B3LYP geometry is by far the one in best agreement with the experiment, the relative errors being generally well within 1% (the largest discrepancy, -1.6%, concerns $d_{\text{O-H}}$). It can finally be noted that the HOH angle is well reproduced and that a and c scale almost according to the experimental ratio $c/a = 1.633$, with all Hamiltonians. Practically the same effect of the employed Hamiltonian on computed equilibrium structures is observed for P-Ice⁴⁴ (here we have no experimental data to compare with).

The problem of the formation energy of the crystal from gas-phase molecules and of the stability of Ice XI relative to P-Ice is more delicate and deserves a detailed analysis. The computed formation energies and cell volumes of both Ice XI and P-Ice, along with the evaluated BSSE, are reported in Table 2 for the three adopted Hamiltonians (HF, PW91, and B3LYP) and the two BSs (BSA and BSB).

Consider first the effect of the Hamiltonian on the computed formation energies. It is seen that PW91 overestimates E^f while

TABLE 2: Computed Formation Energy E^f (kcal/mol), BSSE (kcal/mol) and Cell Volume V (\AA^3) of Ice XI and P-Ice, for Different Hamiltonians and Basis Sets^a

		PW91		B3LYP		HF	
		Ice XI	P-Ice	Ice XI	P-Ice	Ice XI	P-Ice
BSA	E^f	-17.60	-17.72	-14.56	-14.58	-10.40	-10.37
	BSSE	-4.63	-4.38	-3.76	-3.62	-2.97	-2.95
	V	226.48	226.56	244.96	245.44	292.72	293.86
BSB	E^f	-16.77	-16.73	-13.98	-13.92	-10.44	-10.46
	BSSE	-2.41	-2.31	-1.82	-1.76	-0.86	-0.80
	V	241.44	240.64	257.92	258.32	298.87	299.28

^a The experimental formation energy and cell volume of Ice XI are -14.16 kcal/mol and 255.85 \AA^3 , respectively.

HF largely underestimates it; as expected, B3LYP gives intermediate values, very close to the experimental value (-14.16 kcal/mol for Ice XI). The considerable difference in the DFT E^f values with respect to HF (~4 and 6 kcal/mol for B3LYP and PW91, respectively) shows the role of short-range electron correlation in favoring the formation of the crystal from gas-phase molecules. It is also seen that the two structures are essentially isoenergetic at the HF level as already found in previous work,^{6,7} thus confirming the importance of electron correlation in order to correctly predict the minimum energy structure.

All formation energies reported in Table 2 are corrected for BSSE. This correction is seen to be very important, since it can represent as much as 23% of E^f . Furthermore, it must be observed that Crystal looks for the optimum geometry by minimizing the *uncorrected* energy, which means that the corresponding parameters will not represent the "true" equilibrium geometry; it may be expected generally that too compact structures are obtained when BSSE is large. Let us now make some comments on these problems. First notice that, for a given BS, BSSE increases from HF to B3LYP to PW91 and that it is always larger for the ferroelectric than for the antiferroelectric structure; without this correction, the difference in the computed E^f 's, and the extra stability of Ice XI with respect to P-Ice would be even larger. As expected, the computed BSSE considerably decreases when the BS quality is improved; in particular, the HF BSSE becomes very small with BSB (~-0.8 kcal/mol). In all cases, the computed volume is appreciably smaller with BSA than with BSB; this appears to be related to the fact that BSSE is not accounted for in the optimization, as mentioned above. All BSA results are therefore questionable; in particular, since BSSE plays a distinct role in Ice XI and P-Ice, this leads to a *dirty* picture as concerns the relative stability of the two phases. Formation energies (and relative stabilities) calculated with BSB are appreciably less affected by BSSE and justify the similarity with the results obtained by HO in their PW91 study, already noticed (see Table 1). These similarities can also be interpreted in terms of a good description by BSB of the variational occupied subspace. The BSB-B3LYP results are in excellent agreement with the experiment as concerns not only the equilibrium geometry but also the value of E^f and of the relative stability of the two structures.

The present analysis of BSSE effects and of their dependence on BS quality is in agreement with that by Civalleri et al. in a detailed B3LYP study of crystalline urea³⁷ performed with Crystal. Also for that molecular crystal, the use of progressively better BSs resulted in an *increase* of the calculated equilibrium volume, through the reduction of spurious BSSE-dependent intermolecular attractions. In that case, however, the best agreement with the experiment was found with BSs of inter-

TABLE 3: Energy Values at the HF and MP2 Level of the Different Terms Entering the Definition (eq 1) of the BSSE-Corrected Formation Energy E^f ^a

	Ice XI		P-Ice	
	HF	MP2	HF	MP2
E_{cry}/n	-76.071533	-0.225992	-76.071452	-0.225883
$E_{\text{W1}}^{\text{dres}}$	-76.054141	-0.222775	-76.054055	-0.222662
$E_{\text{W2}}^{\text{dres}}$	-76.054131	-0.222696	-76.054051	-0.222700
$E_{\text{W1}}^{\text{bare}}$	-76.052328	-0.222287	-76.052291	-0.222202
$E_{\text{W2}}^{\text{bare}}$	-76.052295	-0.222204	-76.052282	-0.222238
BSSE	-1.14	-0.31	-1.11	-0.29
E^f	-9.03	-2.98	-9.01	-2.93

^a Values are in hartrees in the first five rows and in kcal/mol in the last two rows (1 hartree = 627.509 kcal/mol). Data are reported for both Ice XI and P-Ice and are obtained with BSB.

mediate quality, while the best BSs resulted into too expanded structures. The interpretation of this outcome was that the spurious attraction compensated for the neglect of long-range dispersive interactions, not accounted for by B3LYP. The fact that B3LYP provides very good energetic *and* structural results for ice with our best BS, seems to prove the scarce importance of long-range dispersive intermolecular interactions in this system.

B. HF + LMP2 Results. In this section we report and discuss HF+LMP2 results obtained with BSB for the two ice structures. Since Cryscor does not yet allow automatic geometry optimizations, the first critical point concerns the choice of a reference configuration. We used for this purpose the BSB-B3LYP equilibrium geometries of Ice-XI and P-Ice presented and commented on in section IIIA. Molecular experience supports this assumption, since MP2 and B3LYP equilibrium structures have been found in a number of cases to be very close to each other.⁵³⁻⁵⁶ A more pertinent check has been performed in our parallel paper concerning the vibrational properties of Ice XI in the librational region.⁴⁰ After determining at the B3LYP level the equilibrium configuration and the 12 librational normal modes, we have considered 20 deformations of the crystal regularly spaced along each normal coordinate, up to twice the classical elongation. For such 240 deformed structures we performed HF+LMP2 calculations. After analytical fitting of those data, the minimum energy was found to correspond to an average deformation for each mode with respect to the equilibrium B3LYP geometry of 1% of the classical elongation, that is, almost negligible. Consider finally the case of the isolated water molecule, where full optimization at the HF+LMP2 level is possible, since it involves two parameters only. Again, the results are very encouraging, the equilibrium parameters being as follows (the first entry refers to the HF+LMP2, the second to the B3LYP, the third to the experimental value): $d_{\text{OH}}/\text{\AA}$: 0.961, 0.962, 0.957; $\angle\text{HOH}/\text{deg}$: 104.3, 103.6, 104.5. We note for subsequent reference that the optimized BSB-HF+LMP2 energy of the isolated molecule, corresponding to $E_{\text{W}}^{\text{bare}}$ in eq 1, is -76.055 321 - 0.220 756 hartree (the first entry is the HF energy, the second the MP2 correction).

The values of the other contributions entering the definition of the BSSE-corrected formation energy E^f in eq 1 are reported in Table 3 for the two structures. At the HF level, computed E^f 's are lower and BSSEs larger than those reported in Table 2 because they are referred to the B3LYP equilibrium structures which differ from the HF ones, and in particular are more compact.

The HF+MP2 E^f values (-12.01 and -11.94 kcal/mol for Ice XI and P-Ice, respectively) are underestimated by 2.1 kcal/

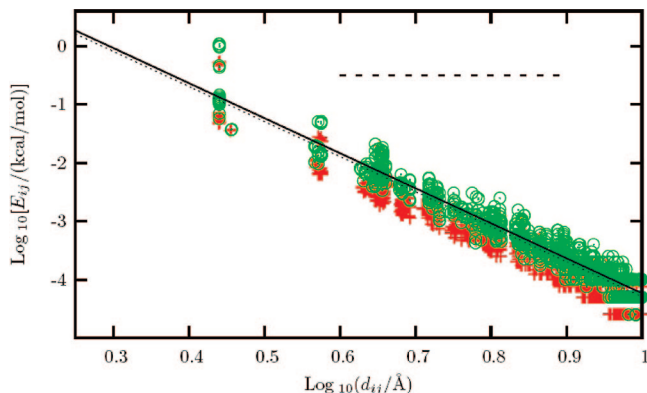


Figure 2. Bilogarithmic plot of pair correlation energies $E_{ij}^{(2)}$ (kcal/mol) for Ice XI (circles) and P-Ice (crosses), as a function of the pair distance d_{ij} (Å). The continuous and dotted straight lines are the respective linear best fits with slope -6 . The horizontal segment represents the range of distances considered for the fit.

mol with respect to the experimental reference. On the other hand, especially due to the MP2 contribution, the stability of Ice XI with respect to P-Ice (0.07 kcal/mol) is very close both to the experimental estimate and to the B3LYP result. We shall discuss these data in the following, after analyzing the role of the different terms in the MP2 energy per cell, $E^{(2)}$. In fact, as anticipated in section IIC, the local-correlation approach allows us to subdivide $E^{(2)}$ into contributions $E_{ij}^{(2)}$ from the different i, j pairs of WFs (i belonging to the reference zero cell) grouped according to different criteria.

Figure 2 reports a bilogarithmic plot of the pair correlation energies $E_{ij}^{(2)}$ as a function of the pair distance d_{ij} for Ice XI and P-Ice. The data are clustered about a (-6) -slope line, according to the expected asymptotic dependence $\propto r^{-6}$ proper of dispersive interactions. The two sets of data have been linearly fitted with the constraint of -6 slope; the d_{ij} range considered is shown in the Figure and corresponds to $4 \div 8$ Å. The best-fit lines are practically coincident for the two structures. From these data the contribution of the dispersive interactions from 13 Å up to infinite distance has been estimated as shown in section IIC; it amounts to 0.009 kcal/mol for both structures and is included in the data of Table 3.

Further insight into the role of the correlation corrections can be gained by distinguishing intramolecular ($E_{\text{intra}}^{(2)}$) from intermolecular ($E_{\text{inter}}^{(2)}$) contributions to $E^{(2)}$, the former resulting from the sum of all $E_{ij}^{(2)}$ terms where i and j belong to the same monomer, and the latter from all others, both divided by the number of molecules in the unit cell. $E_{\text{intra}}^{(2)}$ can be directly compared to the MP2 energy of the “bare” water molecule, $E_W^{(2)} = -0.220\,756$ hartree. For Ice XI we have $E_{\text{intra}}^{(2)} - E_W^{(2)} = +2.47$ kcal/mol, and $E_{\text{inter}}^{(2)} = -5.45$ kcal/mol; the corresponding data for P-Ice are $+2.49$ and -5.42 kcal/mol. In passing from the gas-phase water molecule to the molecule in the lattice, we thus find that there is a partial loss of intramolecular correlation in order to favor the correlation of electronic motions between different molecules. Both terms contribute to the higher stability of Ice XI with respect to P-Ice. A pictorial representation of the different role of correlation terms in the two structures is provided in Figure 3 which reports $\Delta E^{(2)}(d)$ that is, the difference between the correlation energy in Ice XI and P-Ice due to all WF pairs within a distance d . The stabilization of the ferroelectric structure with respect to the antiferroelectric one is seen to be due for about one-half to the different intramolecular correlation energies in the two structures (relative to WF pairs

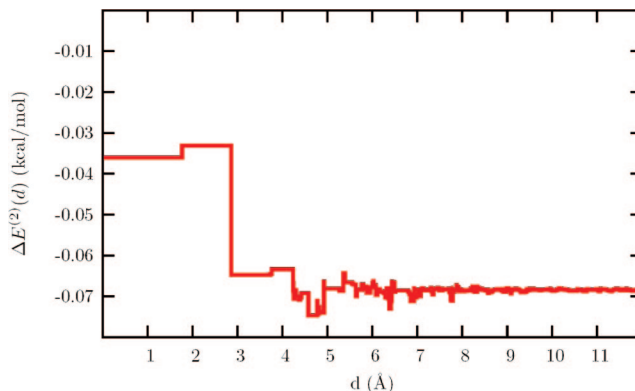


Figure 3. Difference between the MP2 energy of Ice XI and P-Ice due to all WF pairs within a distance d .

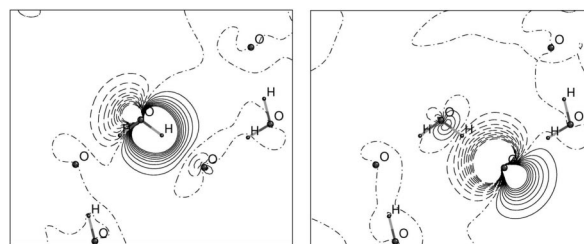


Figure 4. Two-dimensional representation of *bond-like* (left panel) and *lone-pair-like* (right panel) WFs of ice XI. Sections are in a (100) plane through the atoms. Isoamplitude lines are at intervals of $0.01 (e/a_0^3)^{1/2}$. Continuous and dashed lines correspond to positive and negative amplitudes, respectively.

TABLE 4: $E_{\text{c}}^{(2)}$ Contributions to the MP2 Energy of Ice XI Corresponding to WF Pairs of Type b-b, b-lp, and lp-lp Centered in the Same Molecule or in First-Neighbor Molecules^a

		$E_{\text{c}}^{(2)}$	$\Delta E_{\text{c}}^{(2)}$
intramolecular	b-b	-41.166	-0.018
	b-lp	-56.075	-0.027
	lp-lp	-39.117	+0.009
	total	-136.358	-0.036
first-neighbor	b-b	-0.126	+0.002
	b-lp	-0.778	-0.011
	lp-lp	-1.161	-0.020
	total	-2.065	-0.029

^a $\Delta E_{\text{c}}^{(2)}$ is the difference with respect to the corresponding value in P-Ice. All data in kcal/mol.

within at zero distance), for another half-to the correlation of the electronic motions between electrons belonging to adjacent water molecules (the step at ~ 2.7 Å corresponding to the d_{OO} distance); all other contributions are practically equivalent. By concentrating our attention on correlation corrections referring to pairs of WFs belonging to the same molecule or to neighboring molecules, a finer analysis is possible: reference can in fact be made to the WFs involved, either *bond-like* (b) or *lone-pair-like* (lp); the two types of WF are depicted in Figure 4, and are seen to be appreciably localized. As shown in Table 4, intramolecular pair excitations are by far more important, but it is notable that *mixed* (b-lp) terms are about as important as *vertical* b-b and lp-lp ones. As concerns excitations on neighboring molecules, b-b terms are almost negligible, while lp-lp contributions are more important than b-lp ones, in spite of the larger distance between the WFs involved. When comparing these contributions in the two structures, it appears that the higher stability

of Ice XI comes from the intra- and intermolecular terms which most contribute to $E^{(2)}$.

Let us finally reconsider the energy data reported in Table 3. From the above analysis, the extra stability of Ice XI appears to be due to short-range correlation contributions involving electrons on the same molecule or on neighboring molecules. This justifies in a sense the excellent B3LYP result. However, it may be questioned why E^f is underestimated in the present HF+MP2 calculation by as much as 2 kcal/mol. The following considerations can be relevant in this respect. (i) While the molecular reference has been optimized at the HF+MP2 level, the same is not true for the crystalline structures; (ii) the variational description of the virtual subspace is far from complete with BSB; (iii) the MP2 method is just the first step of the *post-HF* techniques for the correct description of electron correlation in both the monomer and the crystal. As concerns point (ii), it can be noted that, for the water dimer, the CP-corrected MP2 contribution to E^f obtained with a BS of quality similar to the present BSB one is underestimated by ~ 0.6 kcal/mol with respect to its limiting value.^{57,58} Instead, a possible overestimation of the MP2-BSSE correction due to the use of the CP procedure as described by eq 1 cannot be invoked in this case, since it amounts to a small fraction of the missing formation energy (~ 0.3 kcal/mol). It may be useful for this purpose to compare the CP-corrected estimate of the MP2 contribution to E^f (-2.98 and -2.93 kcal/mol for the two structures) with the one ($E_{PM}^{(2)f}$) obtained using the PM method briefly described in section IID. In the present context, it is clear that $E_{PM}^{(2)f}$ coincides with $E_{inter}^{(2)}$, defined above as the sum of all $E_{ij}^{(2)}$ terms excluding the intramolecular ones. The values of $E_{inter}^{(2)}$ (-5.45 and -5.42 kcal/mol) would, however, lead to a strong overestimation of the formation energy. As a matter of fact, the hypothesis behind the PM approach that intramolecular correlation terms are not appreciably influenced by the presence of the crystalline environment fails badly in this case.

IV. Conclusions

We have presented an accurate periodic study of the structural and energetic properties of two ice polymorphs performed with DFT techniques and, for the first time, with an *ab initio* HF+MP2 method. Detailed information on the computations (examples of input, BSs, equilibrium geometries) are available on the Web.⁴⁴ Of course, more sophisticated treatments would be welcome, but as it is generally accepted and is confirmed by the recent study by Hermann and Schwerdtfeger,⁴¹ MP2 seems to cover the essential aspects of the correlation energetics for this type of systems. It has been shown that, when it comes to considering very small energy differences as the ones involved here, all computational parameters must be pushed to very tight tolerances, and we have tried to comply with this requirement. In fact, we feel that the most important source of residual error in the present calculations lies in the insufficient quality of the basis set adopted for the *post-HF* calculations. The use of a local approach has allowed us to classify the different contributions to the electron correlation energy according to different criteria. Some conclusions of interest seem to have been reached as concerns this prototypical example of hydrogen-bonded systems:

(i) Dispersive interactions and, more generally, correlation corrections are only important at short-range; again, this result agrees with the finding by Hermann and Schwerdtfeger.⁴¹

(ii) In the crystal, the intramolecular correlation energy is appreciably less than in the isolated molecule, but this effect is more than compensated for by the correlation of electronic motions in neighboring molecules.

(iii) Both effects favor the ferroelectric structure of Ice XI (which is experimentally the most stable) with respect to an antiferroelectric one (P-Ice) taken as representative of ordinary ice.

(iv) In this respect, the results obtained with an accurate GGA-DFT treatment by Hirsch and Ojamäe¹⁷ are confirmed: this could be due to the fact that GGA-DFT satisfactorily describes short-range correlation.

(v) Even better results, both concerning the energetic and the structural aspects and practically coinciding with the HF+MP2 ones, are obtained using the B3LYP hybrid-exchange technique.

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