Explicit Consideration of Vibrational Anharmonicity in Molecular Crystals with Quantum-Mechanical Simulations

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***Abstract*—The vibrations of atoms within a crystalline lattice can give insight into properties of materials. In particular, vibrational anharmonicity is responsible for many critical phenomena, such as thermal effects, specifically in the low frequency range. While vibrational anharmonicity can be measured spectroscopically, quantum-mechanical simulations traditionally can not take anharmonicity into account. In this work, two recently developed methods, the VCI and VSCF models, are used to calculate the explicit anharmonicity in molecular crystals.**

I. INTRODUCTION AND BACKGROUND

CHARACTERIZING vibrational states of solid materials with quantum-mechanical simulations can provide a useful description of spectroscopic and thermodynamic properties. For example, thermal properties such as heat capacity and entropy can be determined from vibrational properties. [1] Traditionally, the potential energy surface (PES) is described by a second-order Taylor series about the equilibrium geometry. This PES is referred to as the harmonic approximation and describes the vibrational states of the lattice as an ensemble of harmonic oscillators. [1] However, the harmonic approximation has several known limitations when describing the lattice dynamics of a crystal, mostly due to the lack of a description of coupled motion within the lattice.

The motion of atoms in a periodic lattice is concerted. To properly describe the coupled atomic motion within a lattice, more terms are required in the Taylor expansion of the PES. The anharmonic expansion of the PES in one dimension is shown below,

$$U(x) \approx \left[U(x) + \frac{U'(x)}{1!}(x - x_0) + \frac{U''(x)}{2!}(x - x_0)^2 \right]_{H.O.} + \left[\frac{U'''(x)}{3!}(x - x_0)^3 + \frac{U^4(x)}{4!}(x - x_0)^4 + \cdots \right]_{A.O.} \quad (1)$$

where x_0 is the equilibrium position and *H.O.* and *A.O.* indicate the harmonic and anharmonic contributions to the potential energy, respectively. Vibrations in the terahertz range are often highly anharmonic and are the most significant contributors to the thermal response of materials. Thus, the development of computational methods that describe the anharmonic vibrational states of materials is important. Unfortunately, deviations from the harmonic oscillator model are difficult to incorporate into *ab initio* simulations. Recently, two new methods were incorporated into a development version of the CRYSTAL code, the vibrational self-consistent field (VSCF) and vibrational configuration interaction (VCI).

The VSCF method involves the interaction of a vibrational mode with the average potential energy of the other modes. The VSCF wave functions can be used as the starting point for the exact coupling of vibrational modes through the VCI. [2] This study presents the results of the anharmonic modal analysis of ice-XI calculated with the VSCF and VCI methods in CRYSTAL.

II. RESULTS

Ice-XI (Figure 1) was chosen as a model system to evaluate these methods due to the abundance of known thermodynamic and spectroscopic data, along with the manageable computation time. The anharmonic PES of ice-XI was calculated using the 6-311G(d,p) basis set and the PBE-D and B3LYP-D density functionals. Initially, the geometry of ice-XI was fully relaxed (lattice vectors and atomic positions) with no constraints other than space group symmetry. Subsequently, vibrational analyses were performed within the harmonic approximation using the well-established methodology involving numerical differentiation. [3], [4] The results of the harmonic simulation are shown for a subset of vibrational modes in Figure 2.

Following the harmonic analysis, the anharmonic corrections were applied. Specifically, the VCI method, which determines the anharmonic frequencies based on not only the explicit anharmonic vibrational potentials, but also couplings between vibrational modes, was evaluated using different levels of mode couplings. In the simplest case, each mode was treated independently (*i.e.*, in the absence of interaction with other modes), which yields the *intrinsic anharmonicity* of each

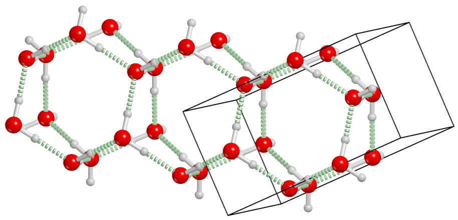

Fig. 1. Structural schematic of ice-XI with the unit cell drawn in black, and hydrogen bonds indicated with green dotted lines.

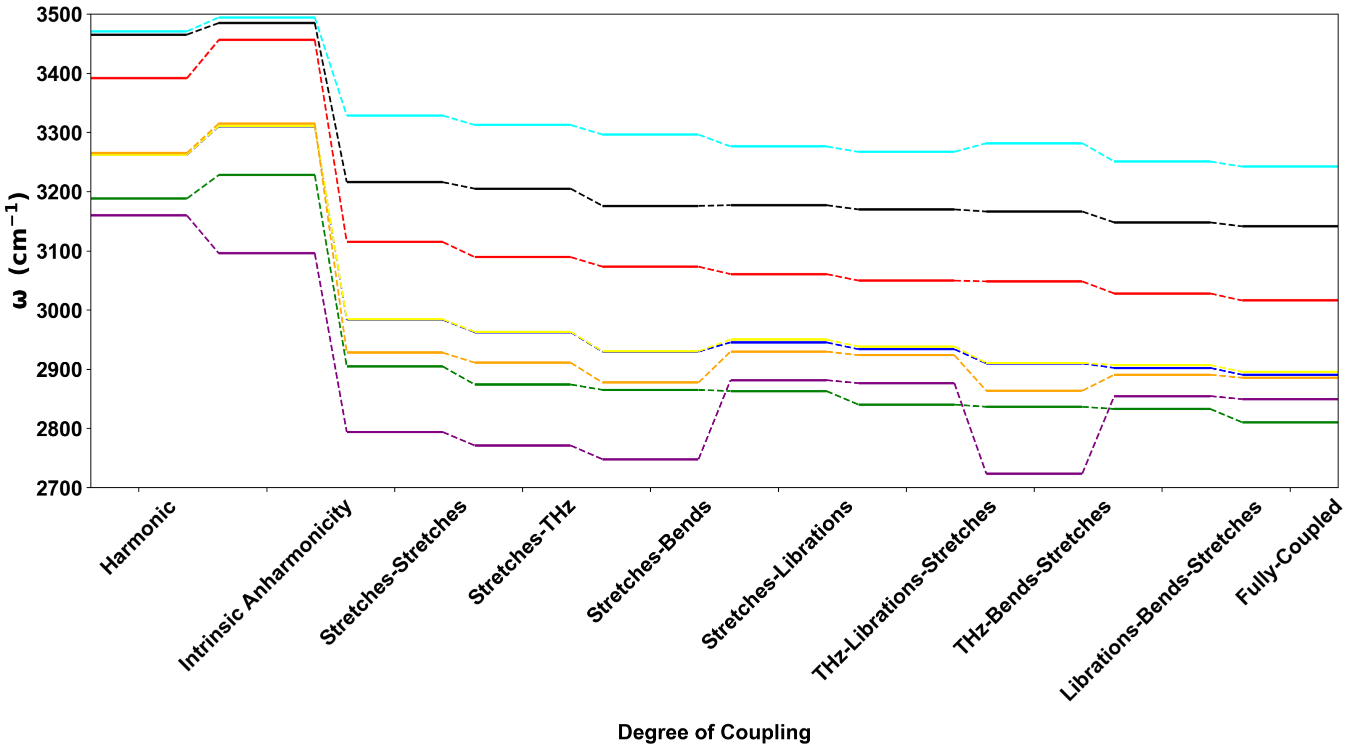

Fig. 2. Vibrational frequency and degree of coupling for the OH-stretching modes of ice-XI.

vibrational mode, with the results shown in Figure 2 for the OH stretching modes. Surprisingly, the intrinsic anharmonic results predict an increase in vibrational frequency for all but one of the modes, which is counterintuitive based on the Morse model.

Subsequently, the vibrations were allowed to couple, with varying levels of allowed interaction. The vibrational modes were grouped based on vibrational mode type and frequency into four categories: THz (0-500 cm^{-1}), librations (500-1500 cm^{-1}), bends (1500-2800 cm^{-1}), and stretches (2800-3500 cm^{-1}). The groups of modes were allowed to interact with each other, first in sets of two (*i.e.*, stretches with stretches, stretches with bends, and so on), followed by allowing three-groups to interact, and finally allowing all modes to interact (*i.e.*, fully-coupled). This analysis not only allows for the evolution of the vibrational frequency with increasing coupling to be obtained, but enables the decomposition of the vibrational coupling into contributions from each set of modes. The results of this analysis are shown in Figure 2, and highlight that based on the level of coupling, a different vibrational frequency is obtained. Of particular note is that once the modes are allowed to interact, the frequency decreases relative to the harmonic *and* the intrinsic anharmonic values, which is the expected behavior. Overall, for the OH stretching modes, increased coupling generally results in a decrease in the vibrational frequency.

III. CONCLUSION

This represents the first demonstration of a fully-coupled VCI simulation of the vibrational properties of an organic solid using a periodic-density functional theory software package. The results of this work enable a detailed understanding of the anharmonic vibrational properties of ice-XI, and provide a framework for future studies into the anharmonic properties of organic solids.

REFERENCES

[1] A. Erba, J. Maul, M. Ferrabone, P. Carbonniére, M. Rérat, R. Dovesi, "Anharmonic Vibrational States of Solids from DFT Calculations. Part I: Description of the Potential Energy Surface", *J. Chem. Theory Comput.*, 15, 3755-3765, 2019.
[2] A. Erba, J. Maul, M. Ferrabone, R. Dovesi, M. Rérat, and P. Carbonniére, "Anharmonic Vibrational States of Solids from DFT Calculations. Part II: Implementation of the VSCF and VCI Methods", *J. Chem. Theory Comput.*, 15, 3766-3777, 2019.
[3] F. Pascale, C.M. Zicovich-Wilson, F. Lopez, B. Civalleri, R. Orlando, R. Dovesi, "The calculation of the vibration frequencies of crystalline compounds and its implementation in the CRYSTAL code", *J. Comput. Chem.*, 25, 888-897, 2004.
[4] C.M. Zicovich-Wilson, F. Pascale, C. Roetti, V.R. Saunders, R. Orlando, R. Dovesi, "The calculation of the vibration frequencies of alpha-quartz: the effect of Hamiltonian and basis set", *J. Comput. Chem.*, 25, 1873-1881, 2004.