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The Role of Anharmonicity and Nuclear Quantum Effects in the Pyridine Molecular Crystal: An *ab initio* Molecular Dynamics Study¹

HSIN-YU KO, Princeton University, ROBERT A. DISTASIO JR., Cornell University, BISWAJIT SANTRA, ROBERTO CAR, Princeton University — Molecular crystal structure prediction has posed a substantial challenge to first-principles methods and requires sophisticated electronic structure methods to determine the stabilities of nearly degenerate polymorphs [1,2,3]. In this work, we demonstrate that the anharmonicity from van der Waals interactions is relevant to the finite-temperature structures of pyridine and pyridine-like molecular crystals. Using such an approach, we find that the equilibrium structures are well captured with classical *ab initio* molecular dynamics (AIMD), despite the presence of light atoms such as hydrogen. Employing path integral AIMD simulations, we demonstrate that the success of classical AIMD results from a separation of nuclear quantum effects between the intermolecular and intramolecular degrees of freedom. In this separation, the quasiclassical and anharmonic intermolecular degrees of freedom determine the equilibrium structure, while the quantum and harmonic intramolecular degrees of freedom are averaging to the correct intramolecular structure. [1] M A Neumann, F J J Leusen, and J Kendrick, *Angew. Chem. Int. Ed.* 47, 2427 (2008). [2] A Otero-de-la-Roza and E R Johnson, *J. Chem. Phys.* 137, 054103 (2012). [3] A M Reilly and A Tkatchenko, *J. Phys. Chem. Lett.* 4, 1028 (2013).

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