

Understanding Vibrational Motions of H⁺ in Hydrogen Bonding via *Ab Initio* Anharmonic Approaches

Jer-Lai Kuo

Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan

[Abstract] Understanding structures and properties of molecular systems bounded by hydrogen bonding has been an interesting and challenging task. The diverse range of interaction strength and intrinsic structural flexibility can be probed directly by vibrational spectroscopic methods. However, vibrational spectra of molecular systems containing proton is often far from trivial partially due to significant anharmonicity. In the last few years, we have been working to understand the vibrational motion of proton in various molecules using the computational algorithms to examine both types of proton (Zundel and Eigen) under different solvation environments. In this talk, we will use solvated H₃O⁺ as an example to demonstrate how we can combine both experimental spectra and *ab initio* anharmonic calculations to extract simpler and clearer pictures to understand the vibrational coupling in the protonated species.

[Introduction] Solvation of proton in hydrogen bond network has been an interesting and important problem in Physics, Chemistry and Biology. To gain a better understanding on the vibrational signatures of H₃O⁺, many previous studies using gas-phase Infra-Red Pre-Dissociation (IR-PD) spectroscopy and high-level *ab initio* calculations have been attempted. IR-PD of H₃O⁺ has been first demonstrated by Lee and coworkers with H₂ tags[1]. subsequently, spectra of H₃O⁺ with one to three Ar, N₂, or CH₄ tags have also been reported. In the frequency range above 3000 cm⁻¹, the main intensity carriers in IR spectra are the fundamental of O-H stretching modes, and their intensities and peak positions are very sensitive to the change in the solvation environments. Furthermore, different types of combinational and overtone modes has been observed depending on the solvation, but there is no clear indication on emergence of these dark states.

Theoretically, one can engage different level of theories to examine the vibrational coupling among different normal modes (NM) and the resulting spectra. Under the NM formalism, the kinetic energy terms are decoupled, and the potential energy component contains most of the anharmonic couplings. We have developed and implemented two *ab initio* anharmonic algorithms that can be applied to compute the vibrational spectra of protonated clusters. In this work, we will use solvated H₃O⁺ as an example to demonstrate how anharmonic algorithms can be applied to assist the assignment of experimentally observed spectra[2,3,4]. Moreover, we can analyze the vibrational coupling among different degrees of freedom to gain a better insight on how the dark (combinational and overtone states) can be activated.

[Methods] In the following, we will summarize our implementations of the two anharmonic schemes. In **Quartic potential (QP)**, all the cubic, and part of the quartic terms are included in the potential energy surface (PES) operator. The vibrational Hamiltonian can be cast into a matrix using direct products of the eigenstates of the harmonic oscillators. After that, the Hamiltonian matrix is diagonalized directly. This way of solving the vibrational problem is known as Vibrational Configuration Interaction (VCI). Furthermore, dipole moment surface (DMS) is approximated by keeping only the linear term, and infrared absorption intensities can be obtained by applying the Fermi's golden rule. Our implementation of QP+VCI has

been applied to study FR of the $(\text{NH}_3)_n$ and $(\text{CH}_3\text{NH}_2)_n$ clusters [5] with a satisfactory agreement with the experimental spectra. **Discrete Variable Representation (DVR)** is another powerful numerical methods to solve partial differential equations. In our DVR implementation, Gauss-Hermite functions were used as basis functions and the potential energy operator is discretized leading to a matrix on the DVR grid. Thus all the high-order terms are kept. In one of our previous works, we found that in $\text{H}_3\text{O}^+\dots\text{Ar}_3$, we can reach a convergence in the eigen-values of less than 2 cm^{-1} using five and seven grid points for the bending and stretching modes, respectively. To summarize, in our implements, the DVR approach includes both electronic and mechanical anharmonicity and QP only considers the latter (with the limitation to up to the 4th order in PES).

[Results and Discussion]

The results of our five-dimensional calculations (by QP and DVR) are compared against the experimental spectra in Figure 1. It is interesting to note that (1) QP+VCI has a better description on the peak position than DVR across all six spectra, and (2) QP+VCI introduces a symmetry breaking of the doubly degenerated state in $\text{H}_3\text{O}^+\dots\text{RG}_3$. The former is clear due to the cancellation of errors, and the cause of the latter will be investigated further by DVR.

Through extensive checking and comparisons[4], we found (1) DVR with 3MR gives a reasonable description of both the peak positions and intensity borrowing, but the truncation at 3MR is found to break the degeneracy of C_{3v} symmetry in $\text{H}_3\text{O}^+\dots\text{RG}_3$. (2) 4MR@DVR is sufficient for the convergence of PES (based on MP2/aDZ). (3) Mixed-Level (2MR based on high-level (CCSD/aTZ)) leads to quantitatively improved agreements.

Good agreements between our *ab initio* anharmonic calculations and experimentally measured spectra on both the Ne-tagged and Ar-tagged species confirm our previous finding [3] that coupling between overtones of bending and fundamental of stretching modes is indeed stronger in Ne-tagged than Ar-tagged H_3O^+ . The reason that overtone in Ne-tagged H_3O^+ is less visible is mainly attributed to the greater mis-matching in the frequency rather than a weak coupling strength. We believe the conclusions drawn from rare-gas tagged H_3O^+ can be generalized and applied to H_3O^+ solvated under other conditions.

[References]

- [1] L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price and Y. T. Lee, *J. Chem. Phys.*, 1989, **91**, 7319
- [2] J-W Li, M. Morita, K. Takahashi, and J-L Kuo, *J. Phys. Chem. A.* **119**, 10887 (2015)
- [3] J. A. Tan, J-W Li, C-c Chiu, H. T. Huynh, H-Y Liao, and J-L Kuo, *Phys. Chem. Chem. Phys.*, **18**, 30721 (2016)
- [4] Q-R Huang, T. Nishigori, M. Katada, A. Fujii, and J-L Kuo, *Phys. Chem. Chem. Phys.* **20**, 13836 (2018)
- [5] Q-R Huang, Y-C Li, K-L Ho, and J-L Kuo, *Phys. Chem. Chem. Phys.*, **20**, 7653 (2018)

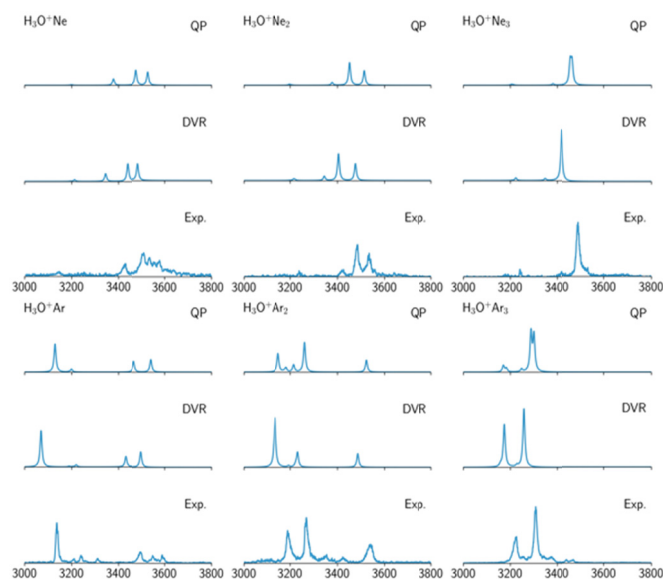


Fig. 1: Comparison of experimental IR-PD of $\text{H}_3\text{O}^+\dots\text{RG}_n$ and absorption spectra simulated with QP and DVR methods.