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Semiclassical Methods for Quantum Nuclear Dynamics in Condensed Phase

Semiclassical methods are based on classical molecular dynamics and they recover quantum mechanical effects by summing the contribution over all the classical paths of the Feynman Path Integral propagator. In Miller's semiclassical initial value representation (SCIVR)[1] formulation of the Herman-Kluk propagator, the sum over frozen guassian wavepackets reproduces quantum effects, including zero point energies, tunneling and quantum anharmonicity. The Milan Semiclassical Group has implemented SCIVR for nuclear spectra calculations up to as many degrees of freedom as in a typical condensed phase simulation. In this presentation I will show how our ab initio divide-and-conquer "on-the-fly" QM/MM semiclassical molecular dynamics approach[2-4] is able to reproduce the experimental IR spectra of thymidine in water and that one of formic acid adsorbed on Anatase (101) surface, as a prototype adsorption reaction of gas Brønsted acid on oxides. In the first case, we show the importance of solute-solvent reciprocal polarization effects that the molecule and the water solvent exert on each other, and nuclear zero-point energy effects. In the second case reported in the picture below, we find that the acid proton forms an extraordinarily short and strong hydrogen bond with the surface oxygen, that can be compared to that one of ice at high pressures. We believe that this is at the root of a substantial redshift with respect to the typical free OH stretching frequency, which eludes its straightforward detection. In conclusions, I will show how our semiclassical methods are an accurate and practical tool to study quantum vibrational spectroscopy in solution and condensed phase, incorporating high-level and computationally affordable descriptions of both electronic and nuclear problems. Possibly, I will also show possible future developments[7] about vibrational dynamics. [1] W. H. Miller, J. Phys. Chem. A, 2001, 105, 2942-2955 [2] M. Ceotto, G. Di Liberto, R. Conte, Phys. Rev. Lett., 2017, 119, 010401 [3] R. Conte, G. Mandelli, G. Botti, D. Moscato, C. Lanzi, M. Cazzaniga, C. Aieta, M. Ceotto, Chem. Sci., 2025, 16, 20-28 [4] R. Conte, C. Aieta, M. Cazzaniga, M. Ceotto, J. Chem. Phys. Lett., 2024, 15, 7566-7576 [5] D. Moscato, G. Mandelli, M. Bondanza, F. Lipparini, R. Conte, B. Mennucci, M. Ceotto, J. Am. Chem. Soc., 2024, 146, 8179-8188 [6] E. Fallacara, F. Finocchi, M. Cazzaniga, S. Chenot, S. Stankic, M. Ceotto, Angew. Chem. Int. Ed., 2024, 63, e202409523 [7] M. Ceotto, J. Chem. Phys., 2025, 162, 064108

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