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Signatures of Coherent Vibrational Energy Transfer in IR and Raman Line Shapes for Liquid Water[1] MINO YANG, Chungbuk National University, JAMES SKINNER, University of Wisconsin-Madison — We calculate theoretical IR and Raman line shapes for the OH stretch region of liquid water, using the mixed quantum/classical and electronic-structure/molecular-dynamics methods. Our approach improves upon the time-averaging approximation used earlier for the same problem, and our results are in excellent agreement with experiment. Previous analysis of theoretical results for this problem considered the extent of delocalization (over local OH stretch excitations) of the instantaneous vibrational eigenstates. In this work we present a complementary analysis in the time-domain, by decomposing the appropriate response functions into diagonal and off-diagonal contributions (in the local mode basis). Our analysis indicates that all vibrational spectra show signatures of coherent vibrational energy transfer. This is manifest in different (IR, isotropic and depolarized Raman) experiments to different extents, because of the competition between coherent energy transfer and rotational disorder.

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