Vibrational energy relaxation rate constants in liquid solutions via the linearized semiclassical method

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I will review my group’s work over the last decade on the calculation of vibrational energy relaxation (VER) rate constants in liquid solutions via the linearized semiclassical (LSC) method. Two computational implementations of the method will be presented. The accuracy and reliability of the LSC method and its ability to capture nontrivial quantum effects will be demonstrated by applications to a variety of liquid solutions, including liquid O$_2$, liquid N$_2$, liquid O$_2$/Ar mixtures, H$_2$ dissolved in liquid Ar and CX$_2$ (X = O, S, Se) dissolved in liquid Ar and liquid Ne. A more recent application to liquid HCl will be discussed in more detail. In this case, the LSC VER rate constant is found to be in excellent agreement with experiment and the electrostatic force is found to contribute significantly to it. In contrast, the corresponding classical VER rate constant is found to be two orders of magnitude slower than the experimental value and is dominated by the Lennard-Jones forces. These observations suggest that quantum delocalization, enhanced by the light mass of hydrogen, amplifies the contribution of repulsive Coulomb forces, thereby making electrostriction an unlikely mechanism for VER in the case of hydrogen stretches. This interpretation is reinforced by calculations of the VER rate constant in liquid DCl. In this case the quantum enhancement of the VER rate constant is observed to be greatly diminished in comparison to HCl, thereby giving rise to a reversal of the isotope effect in comparison to that predicted by the corresponding classical treatment (i.e. whereas the classical VER rate of DCl is faster than that of HCl, the opposite trend is predicted by LSC). It is also shown that VER of DCl is completely dominated by the Lennard-Jones forces within either classical or LSC treatments, thereby suggesting that electrostriction is the underlying mechanism in this case.