VIBRATIONAL ENERGY RELAXATION OF CHOLOROIODOMETHANE IN COLD ARGON

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Electronically exciting the C-I stretch in the molecule chloroiodomethane CH_2ClI embedded in a matrix of argon at 12K can lead to an isomer, iso-chloroiodomethane CH_2Cl-I, that features a chlorine iodine bond.[a] By temporally probing the isomer at two different frequencies of 435 nm and 485 nm, multiple timescales for isomerization are inferred. To gain further mechanistic insights into this process we have studied the isomerization theoretically using molecular dynamics. Two and three low frequency modes (C-Cl-I bend, Cl-I stretch and C-Cl stretch) are included in the model. The experiment is simulated by equilibrating the molecule in the parent configuration and providing an energy of 37,500 cm^{-1}, corresponding to the electronic excitation of the C-I stretch. Subsequent time evolution of the classical trajectories is monitored, and the decay rates of energy are compared to the experimental spectroscopy results. Varying different parameters related to the potential energy surface can lead to different results and their implications to the energy flow are discussed. The decay rates in the isomer well are also compared to the classical Landau Teller theory.

[a] T. J. Preston, M. Dutta, B. J. Esselman, A. Kalume, L. George, R. J. McMahon, S. A. Reid, and F. F. Crim, J. Chem. Phys. **135**, 114503 (2011)