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 20K can lead to an isomer, iso-chloroiodomethane CH_2Cl-I, that features a chlorine iodine bond [T. J. Preston *et al.*, J. Chem. Phys. **135**, 114503 (2011)]. By temporally probing the isomer at two different frequencies of 435 nm and 485 nm, three timescales for isomerization were inferred. The first and second timescales correspond to formation and initial relaxation of the isomer, with a decay rate of 0.45 ps^{-1}. The third timescale is attributed to further energy loss as the molecule cools to its local minima, with a decay rate of 0.07 ps^{-1}. To gain further mechanistic insights into this process, we studied the isomerization theoretically using molecular dynamics. Initial energy of 37,500 cm^{-1} (corresponding to electronic excitation of C-I stretch) is provided to the C-I bond. As in the experiment, three timescales are observed. First the molecule loses energy through collisions with a few argon atoms, which leads to a loss of about 10,000 cm^{-1} in 100 fs. Subsequent energy loss follows a bi-exponential decay, with decay rates of 1.16 ps^{-1} and 0.21 ps^{-1}. The implications of our results to the interpretation of the spectroscopic results will be discussed.