

Vibration Induced Bond Formation and Breaking

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The high overtone induced processes are initiated by promoting a molecule or a complex to chemically relevant energies in high vibrational excited states through the thermal excitation or direct absorption of visible (VIS) or near-infrared (NIR) radiation. Unlike the thermally induced processes, the reactions initiated by vibrational overtone-pumping of ground electronic state molecule through direct absorption of photon can be treated without the need to consider the collisional activation processes. In general, it is required that the energy is deposited into the initially excited vibrational state and subsequently transferred by intramolecular vibrational redistribution (IVR) to other modes of the molecule including the reaction coordinate. For example, it has been demonstrated that high overtone excitation of OH groups in carboxylic acids isolated in low temperature matrices leads to two different unimolecular processes: isomerization and/or decomposition of the molecules [1-4]. Moreover, overtone pumping was used, for example, in the case of formic acid dimers to produce high-energy conformers within the hydrogen-bonded complexes [5-7].

Studying formic acid-water complex via computational methods hints, that overtone vibrations in formic acid OH-bond induce hydrogen exchange with water molecule. We discuss details of computations and how bonds form and break during the reaction.

References

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