Probing IR-Raman rovibrationally excited HCl molecule with X-ray spectroscopies : a theoretical approach

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Up to now, most of the experimental Pump-Probe devices developed to control bond dissociation routinely combine infrared frequencies (pump) and UV (probe) light frequencies. Only recent theoretical studies [1, 2] have simulated the X-ray absorption spectra of small molecules driven by strong IR pulse, the association of an IR-pump with a X-ray probe radiation being today unexplored experimentally. In the present work, we show detailed calculations of a new scheme for time control of bond dissociation. The scheme combines far-off-resonant Raman transitions [3] initiated by one chirped and one monochromatic laser pulse, with X-ray spectroscopies. The main purpose of this study is to show through a theoretical approach taking into account the rotation of the molecule, that such a pump-probe association provide a powerful tool to control dynamics of molecular dissociation through a core-binding energy analysis. An experimental scheme is then proposed, where : (1) selected vibrational states are populated by infrared (IR) laser pulses following the Raman Chirped Adiabatic Passage technique [3]; (2) the evolution of the population of the different vibrational states is tracked by following the variation of the X-ray absorption or photoelectron spectrum of the molecule. Beyond opening a unique opportunity for probing the potential surfaces of the ground, core-excited, and final molecular states [4], this technique provides a time-control of bond dissociation through modulation of core hole chemical shift with high resolution [5, 6].

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