Resonant Stimulated X-Ray Raman Spectroscopy of Molecule Following Core Ionization

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Abstract We investigate computationally the valence electronic excitations of the amino acid glycine following a sudden nitrogen core ionization induced by an attosecond X-ray pump pulse. The molecule left in a superposition of cationic excited states is then probed by a second broadband X-ray pulse together with a narrowband pulse tuned to the carbon K-edge. Transient X-ray absorption and attosecond stimulated X-ray Raman signals are simulated and related to the evolution of the valence excited state wavepacket.

1 Introduction

A sudden ionization by removal of a core electron, which is faster than the electron correlation time, can bring molecules to a superposition of large number of cationic states. A typical response time for spectator electrons to a sudden removal of an electron is about 50 as [1, 2]. The sudden-ionizing pulse should therefore be shorter than this time. With the development of attosecond pulses [3], sudden ionization is becoming feasible.

After an electron has been ejected from the core orbital, the molecule is prepared in a nonstationary state [4] which can be monitored by attosecond stimulated X-ray Raman spectroscopy (ASRS). Core excitations are spatially selective because core transitions for different types of atoms are spectrally well removed from each other [5]. In an X-ray Raman process [6–8], only those valence excitations with transition density in the region near the selected atom will be active.

In vibrational spectroscopy, femtosecond stimulated Raman spectroscopy (FSRS) [9, 10] has been widely used to monitor nuclear dynamics. This technique uses a combination of narrow and broadband pulses to collect the Raman signal in a single shot. ASRS extends FSRS to the X-ray regime. We further use resonant

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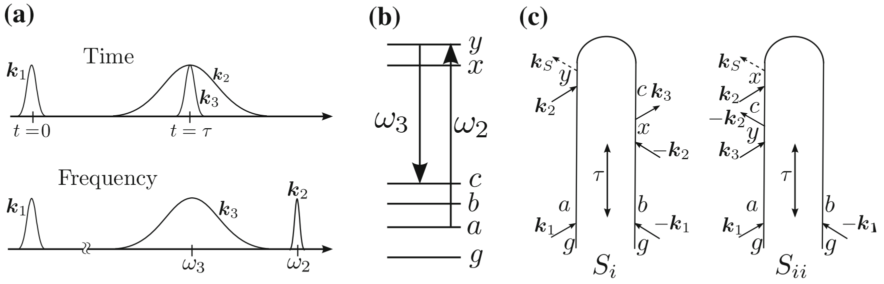

Fig. 1 **a** Pulse sequence for the narrow pump/broad probe stimulated Raman experiment. **b** Level scheme. **c** The two contributing loop diagrams

rather than off-resonant pulses. In an ASRS experiment, two probe pulses hit the sample simultaneously. The first is narrowband (long in duration) and resonant with a core transition, and the second probe is broadband (short in duration), and red-shifted from the first, as shown in Fig. 1. The signal is given by the spectrally dispersed transmission of the broadband pulse. We neglect nuclear motion in these calculations. The short lifetime of the initial ionized state ($\Gamma_{ab} = 0.09\,\text{eV} = \hbar/7.3\,\text{fs}$ [5]) means that the entire signal is collected on a timescale that is very fast in comparison to nuclear motion.

2 Results and Discussion

In Fig. 2 we show the electron density difference in glycine, defined as the time-dependent density of the cation minus the ground state electronic density, for five different times following core ionization of nitrogen. The large number of states with nonnegligible amplitudes in the superposition indicates a collective electronic motion. The negative region surrounding the nitrogen atom represents the removed electron. Positive electron density regions surrounding the nitrogen correspond to relaxation of the system in the presence of the hole. The fact that this relaxation is not negligible at short time delays is attributed to the truncation error of the eigenstate basis used to project the initial state. A truncated basis must be used since the Raman signal scales as the number of valence-states cubed. Considerable changes in the electronic density in the region around the two carbon atoms is seen for interpulse delays $\tau = 110.1$ and 317.2 as. For delays of 216.8 and 424.7 as the density changes around the carbon atoms is diminished. This matches the changes in intensity seen in the time-dependent ASRS signal in the right column of Fig. 2. Large differences in the density around the carbon atoms corresponds to larger carbon K-edge Raman signal, and small differences likewise lead to smaller signals.

It should be emphasized that even though the time delay between the ionizing pulse and the broadband Raman probe is well defined, the resulting signal may not be viewed as an instantaneous snapshot of the Raman spectrum, but is averaged

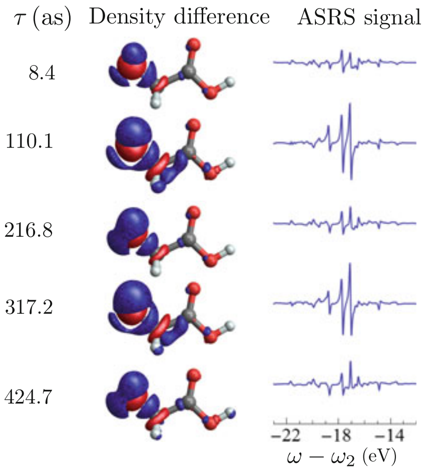

Fig. 2 Density difference for the state following ionization, defined as the time-dependent density minus the ground-state density for the cationic wavepacket, at time delays which correspond with the maxima and minima for the Raman peak at $\omega - \omega_2 = -17.2\,\text{eV}$ alongside the corresponding ASRS signals. *Red* isosurfaces show negative density differences, and *blue* surfaces show positive difference. The nitrogen atom is hidden by the *red* surface, corresponding to the suddenly created core hole

over the dephasing time of the final state. Correspondence between the time-dependent ASRS signal and changes in the electronic density are seen for short times following ionization. However, the ASRS signal depends upon the multi-electron dynamics, while the density is a single-electron property and not as sensitive to interference effects, so correspondence at later times is not as obvious.

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