Ultrafast transient-grating study of molecules after high intensity excitation

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Abstract: We report a method based on transient-grating spectroscopy to assess the degree of alignment and electronic state mixing caused by intense femtosecond laser pulses. Molecular deformations are determined by analysis of the filed-free rotational recurrences.

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1. Introduction

High-intensity off-resonance laser fields from ultrafast laser pulses can cause very large electric-field gradients. Molecules experience a large torque along the polarization vector of the field due to the anisotropic polarizability. With long laser pulses the torque is enough to cause adiabatic alignment [1, 2], however, with ultrafast pulses the torque provides an 'instantaneous' kick towards alignment [3]. For high enough fields, electronic state mixing can occur. When the electronic states have different geometry, this process leads to molecular deformation. For our measurements, we use two high-intensity laser pulses followed by a weak probe pulse. The signal corresponds to the diffraction of the probe laser from the transient grating formed by the two intense pulses [4]. The degree of molecular alignment and deformation are measured from changes in the rotational recurrences that are observed after field-free evolution of the molecular sample.

2. Experimental

The experiments were carried out with three laser beams in the forward-box geometry. The first two laser pulses where overlapped in time while the third pulse was delayed by a computer controlled actuator. The intensity of the first two laser pulses was varied between 10^{10} to 10^{12} W/cm^2 using a set of matched neutral density filters, all with the same thickness. The third pulse was maintained at a fixed 10^{10} W/cm^2 intensity. The signal was collected background-free at the phase matching geometry. The sample consisted of a quartz cell containing CS_2. A cold finger in the cell was kept in ice to reduce the vapor pressure to 100 Torr. The 60 fs laser pulses were centered at 620 nm.

3. Results

The full rotational recurrence of CS_2 is expected at 76.5 ps [4, 5]. When the laser pulses are weak, this feature can be observed and an accurate rotational constant can be determined for the linear molecule [4, 5]. In Fig. 1a, we show experimental data for the case when all laser pulses were weak. The simulation of the data with no adjustable parameters fits well the experimental results (see Fig. 1a). When the laser intensity of the first two pulses is increased by an order of magnitude, the full rotational recurrence observed increases in intensity. The data can still be fitted by a room temperature distribution of linear CS_2 molecules (see Fig. 1b).

When the intensity is increased above 10^{12} W/cm^2, the full rotational recurrence increases in intensity and changes shape (see Fig. 1c). Most markedly, the first feature increases in intensity by a factor of two. The features observed at long time delays, >77.5 ps, increase in intensity and new oscillations are observed. This region of the transient is amplified by a factor of five in the figure.

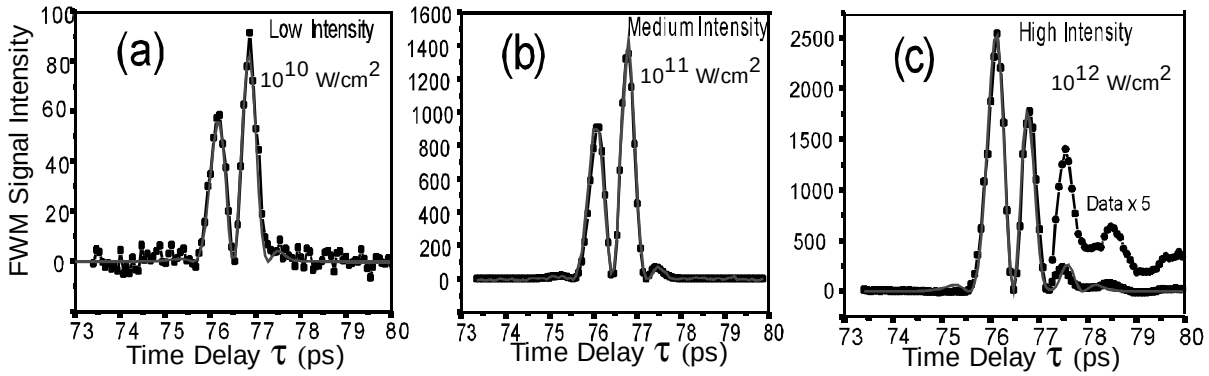

Figure 1: Experimental data and simulations of transient-grating measurement on gas phase CS_2. The first two laser pulses are overlapped in time and their peak intensity is regulated from (a) weak, to (b) medium, to (c) high. The effect of the high-intensity laser field on the molecules is measured after a long time delay by the probe pulse, here we only show the time delay where the first full-rotational recurrence takes place. Note that for weak and medium intensity the data can be fit by a simulation without adjustable parameters. However, for high intensity fields the shape of the recurrence changes. Simulation of the high intensity transient includes bent CS_2 molecules.

Simulation of the data for high intensity excitation shown in Fig. 1c, requires the inclusion of bent CS_2 molecules. The bending is thought to occur as a result of mixing between the linear ground state and the bent excited state.

4. Discussion

We explore the alignment and deformation induced by high-intensity off-resonance laser pulses on gas phase CS_2 molecules. When the laser intensity is ~ 10^{10} W/cm^2, the data can be fit without adjustable parameters. For intermediate intensities, a large increase in the signal is observed, this enhancement results from the initial torque towards alignment that the molecules experience. Beyond 10^{12} W/cm^2, the structure of the rotational recurrence changes. The data could only be simulated in this case by including bent molecules. In conclusion, we consider the ultrafast transient-grating technique to be ideal to measure the changes that molecules experience in the presence of high-intensity laser pulses.

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