



# Intense pumping and time- and frequency-resolved CARS for driving and tracking structural deformation and recovery of liquid nitromethane molecules



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## ABSTRACT

A modified CARS technique with an intense nonresonant femtosecond laser is presented to drive the structural deformation of liquid nitromethane molecules and track their structural relaxation process. The CARS spectra reveal that the internal rotation of the molecule can couple with the CN symmetric stretching vibration and the molecules undergo ultrafast structural deformation of the CH<sub>3</sub> groups from 'opened umbrella' to 'closed umbrella' shape, and then experience a structural recovery process within 720 fs.

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## 1. Introduction

The interaction between molecules and intense femtosecond laser fields has been investigated actively [1]. For diatomic and small-sized polyatomic molecules, some phenomena, such as high-order harmonic generation, above threshold ionization, double ionization, Coulomb explosion (CE), and dissociative double ionization, can be induced by intense laser field with the intensities beyond  $\sim 10^{12}$  W/cm<sup>2</sup>, which have been investigated intensively by using time-of-flight mass spectroscopy (TOFMS), two-dimensional imaging based on the TOFMS, and ion-imaging [2]. Intense nonresonant laser field of ultrafast laser pulse can apply torques on molecules due to the interaction between the induced dipole moment and the laser field itself [3]. The torque can produce an 'instantaneous' kick on the molecule and therefore induce molecular alignment and deformation [4,5]. The geometrical structure of molecules can become deformed within 100 fs [6]. The molecular dynamics prior to CE can only be indirectly deduced from the distribution of fragment ions because the TOFMS and ion-imaging methods mainly determine the dissociation pathway by detecting the major, submajor, and minor products fragment ions. In

essence, these methods are destructive and complex. Besides, they require the sample to be in the gas phase, so the information of the molecules in the liquid phase under the intense nonresonant femtosecond laser has not been provided based on these studies. It is challenging to monitor molecular structural deformation in real time driven by intense nonresonant laser in the liquid phase under the noninvasive condition. Actually the physical mechanism of molecular deformation induced by intense laser is dynamic Stark effect [7]. Sussman et al. reported a hybrid combination of two limits of Raman scattering to monitor the process of molecular alignment and angular momentum orientation of molecular hydrogen [8]. In this experiment, the probe beam and signal are arranged in the same direction and so the signal–noise ratio is unsatisfactory. In order to improve the signal–noise ratio, a modified time-resolved coherent anti-Stokes Raman scattering (CARS) spectroscopy technique is presented in this Letter. It is well known that CARS is a powerful technique for detecting vibrational features of complex molecules in the liquid phase and sensitive to structural changes in the molecules [9,10]. It is a kind of nonlinear four-wave mixing process in which a pump ( $\omega_p$ ) pulse, a Stokes ( $\omega_s$ ) pulse and a probe ( $\omega_{pr}$ ) pulse interact with a sample and generate an anti-Stokes signal at the frequency of  $\omega_c = \omega_p - \omega_s + \omega_{pr}$  [11]. Its significant advantages over other methods originate from its nondestructive and nonintrusive features and the background-free nature of signal detection by the phase-matching conditions [12,13]. In the conventional CARS experiments, the intensity of the pump laser is kept low

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to avoid the reactions or supercontinuum induced by the pulses. In our experiments, an intense femtosecond pulse ( $\sim 10^{12}$  W/cm<sup>2</sup>) is used to drive the molecular deformation, and the time-resolved anti-Stokes signals are collected to observe the structural relaxation process. The results indicate that the evolution of molecular structural deformation can be clearly detected from the CARS spectra. It provides a powerful tool to study the molecular dynamics process in real time.

As one of the simplest organic-nitro compound as well as an important energetic material, nitromethane (NM) with the chemical formula CH<sub>3</sub>NO<sub>2</sub> has been extensively studied for decades [14]. NM is liquid under the room temperature and atmospheric pressure. To our knowledge, study about NM molecules in the liquid phase interacted with intense nonresonant femtosecond laser field has not been reported yet. In this Letter, we perform the intense pumping and time- and frequency-resolved CARS experiments on liquid NM and successfully track the structural deformation induced by the nonresonant femtosecond laser. The phenomenon of some new vibrational modes converging with the delay time is observed in our experiment, which is ascribed to the structural deformation and relaxation of NM molecules induced by the laser field.

## 2. Experimental

In this modified CARS experiment, the intensity of pump laser pulse is intentionally set at high intensity of  $\sim 10^{12}$  W/cm<sup>2</sup> to induce structural deformation of NM molecules in the liquid phase, and at the meantime to keep it below the threshold of CE for avoiding quick CE. The main apparatus of our experiment have been described in other paper [15]. Briefly, a 110 fs, 1.0 mJ, and 800 nm pulse from a 1 kHz Ti: sapphire amplifier is employed. The output pulse is split into two beams by a beam splitter (9:1). The 90% beam is divided into two parts equally. One of them is used as the intense pump pulse, and the another is broaden to be ps by a narrow band pass filter as probe beam with line width of  $\sim 1$  nm. The 10% beam produces a supercontinuum (SC) pulse by passing an Al<sub>2</sub>O<sub>3</sub> crystal as the Stokes pulse [16]. The SC pulse has an ultrabroadband spectral profile, ranging from 400 nm to 1100 nm. The pump pulse with the optimized energy of 5  $\mu$ J obtained from the intensity test experiment is focused by a 175 mm focal length lens. The intensities of Stokes and probe pulses are set much lower

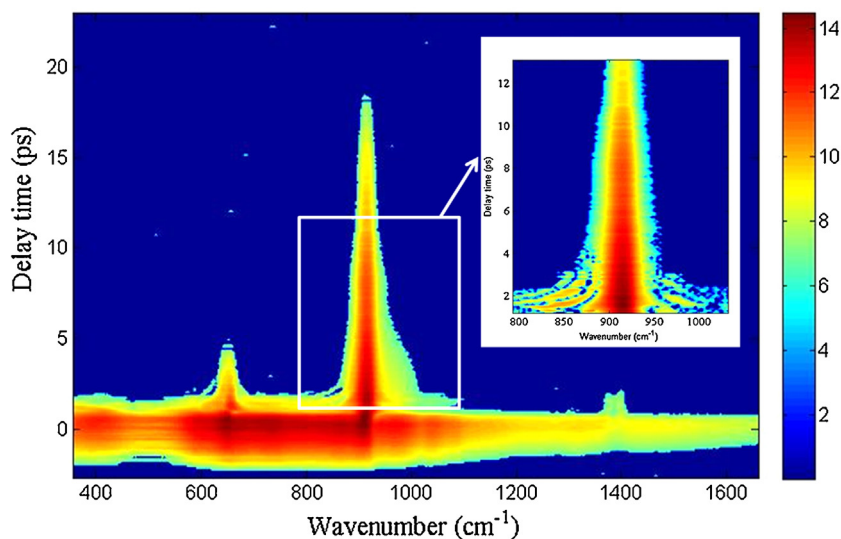
than the pump pulse. Two delay lines are motorized by a motion controller. One delay line is used to produce the temporal overlap of the pump and Stokes pulses by changing the delay time between them. Another one provides the variable delay time for the probe pulse. The folded BoxCARS geometry is used, in which the properly chosen angles between the beams, are determined by the four-wave-mixing phase-matching condition [17]. All three beams are sent through a lens focused onto the sample of liquid NM filled in a quartz glass cuvette of 1 mm thickness. And a collecting lens sends the signal to the CCD spectrometer. The signals are generated in a direction of  $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{St}} + \mathbf{k}_{\text{pr}}$  [18]. The characteristic vibrational mode of NM molecule (917 cm<sup>-1</sup>) is chosen to be excited. According to the conservation of energy and momentum, the near-infrared wavelength component of SC at 860 nm is used as the Stokes pulse, and then the CARS signal wavelength is around 745 nm. All measurements are taken at the room temperature (295  $\pm$  3 K). The analytical pure liquid NM is used in the experiment without further purification.

## 3. Results and discussion

A contour plot of time- and frequency-resolved CARS data from liquid NM under intense nonresonant femtosecond laser field is depicted in Figure 1. The CARS signal is centered at the position of about 917 cm<sup>-1</sup>, and covers the region from 400 to 1600 cm<sup>-1</sup>. Generally, the molecules are considered as quantum systems while the femtosecond laser pulses are treated as classical electromagnetic fields to clarify the signal. According to the theory of nonlinear optical spectroscopy, the experimentally detected CARS signal intensity is formulated as [19–21]:

$$S_c(t) \propto \int_{-\infty}^{+\infty} |P_c^{(3)}(t, \tau)|^2 d\tau, \quad (1)$$

where  $P_c^{(3)}$  denotes the nonlinear polarization,  $t$  is the delay time between the probe pulse and the synchronous pump and Stokes pulses. It consists of the fast nonresonant part due to the response of the electronic system and the slow resonant part corresponding to the response of the vibrational modes. As shown in Figure 1, the nonresonant part creates an intense signal at zero delay time ( $t=0$ ) when all the three pulses overlap in space and time. After about 1 ps delay time, the nonresonant contribution in the CARS spectra is negligible. According to the spontaneous Raman modes



**Figure 1.** Contour plot of CARS spectra on a log scale for liquid NM. The two axes represent delay time and Raman vibrational frequency values. The inset shows the data has been dealt with by subtracting their lower envelope to see the converging structure clearly.

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