Measurement of Second Hyperpolarizability and Nuclear Rotational Response of Gas-phase Carbon Disulfide

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Abstract: We use nonlinear beam deflection to separate the bound-electronic and nuclear-rotational responses in gas-phase CS_2. This allows a direct comparison of the second hyperpolarizability to our liquid CS_2 measurements considering local-field effects.
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1. Introduction

The nonlinear optical (NLO) response of a gaseous medium under an intense laser field has been extensively studied and knowledge of the precise magnitudes and temporal dynamics of the third-order nonlinear refraction (NLR) are critical for various applications including filamentation. The total NLR response of gas-phase molecules excited by an ultrashort pulse are governed by a nearly instantaneous response that originates from the bound-electronic second hyperpolarizability, and a non-instantaneous response from field-induced nuclear rotation due to two-photon stimulated Raman transitions [1]. As a widely used NLO standard material, carbon disulfide (CS_2) has been thoroughly studied in its liquid form, where the major NLR responses are characterized by a bound-electronic Kerr index $n_{2,el}$ plus three major nuclear contributions [2]. The macroscopic $n_{2,el}$ is related to the real part of the orientationally averaged microscopic second hyperpolarizability γ_s via the molecular number density N and a third-order Lorentz local-field factor $f^{(3)}$ by eq. (1) [4], where c is the speed of light in vacuum, ε_0 is the vacuum permittivity, and n_e and n_p are the real linear refractive index of excitation and probe respectively.

$$\mathrm{Re}[\gamma_s] = \frac{4\varepsilon_0^2 c n_e n_p}{3 N f^{(3)}} n_{2,el},\tag{1}$$

An approach to measuring the hyperpolarizability without the need for local-field corrections is to directly measure nonlinear refraction in the gas phase where negligible local-field effects are present ($f^{(3)} \sim 1$). In this work, we expand upon our recently developed beam deflection technique [3] to measure NLR transients of gas-phase CS_2 using femtosecond pulses. The bound-electronic and nuclear rotation responses are separated, allowing an unambiguous determination of the $\mathrm{Re}[\gamma_s]$, which makes possible direct comparison to the $\mathrm{Re}[\gamma_s]$ obtained from our liquid-phase measurements [2].

2. Experiment and Results

The beam deflection technique uses a focused strong excitation beam to induce a refractive index change in the sample that follows its spatially Gaussian irradiance profile [2, 3]. The probe pulse is focused ~5× smaller and is displaced to where the index gradient is largest, as shown in Fig. 1a. The refractive index gradient induced by the excitation acts as a prism deflecting the probe beam by a small angle. The CS_2 vapor (Sigma-Aldrich, 270660, ≥99.9% purity) is contained in a 100 mm path length cell such that the beams to not overlap at the cell windows. The beam crossing geometry is illustrated in Fig. 1b, where the excitation crosses the probe in the vertical (yz) plane, but is displaced in the horizontal (xz) plane, as shown in Fig. 1c, causing deflection in the x-direction. In this experiment we use ~10mJ, ~40 fs (FWHM) pulses at a 1 kHz repetition rate from a Ti:Sapphire amplified laser system (Coherent Legend Elite Duo HE+) to pump an optical parametric amplifier (TOPAS-HE) to produce excitation pulses at 1250 nm. A portion of the excitation is used to generate a white-light continuum (WLC) in a 5 mm thick sapphire plate, which is then spectrally filtered by bandpass interference filters ($\Delta\lambda$ = 10 nm FWHM) at 950 nm to use as probe. The probe is detected by a quad-segmented Si photodiode (OSI QD50-0-SD) placed in the far-field. The difference in energy falling on the left and right sides of the segmented photodiode as shown in Fig. 1c $\Delta E = E_{left} - E_{right}$, is measured using lock-in detection and normalized to the total energy E, yielding the deflection signal $\Delta E/E$. In the small signal limit, $\Delta E/E$ is proportional to the refractive index change Δn [3]. By temporally delaying the excitation and probe, NLR transients can be resolved, and by varying the polarization angle between the excitation and probe, the tensor symmetry of the nonlinear susceptibility is measured. At the magic angle (~54.7°) the nuclear rotation response is eliminated, which isolates the bound-electronic NLR and enables direct measurement of $\mathrm{Re}[\gamma_s]$.

Fig. 1d shows the measured $\Delta E/E$ of gas-phase CS2 with its polarization dependence, which consists of an instantaneous bound-electronic response (Δn_{el}) at zero delay and a slowly rising rotational response (Δn_{rot}) with a
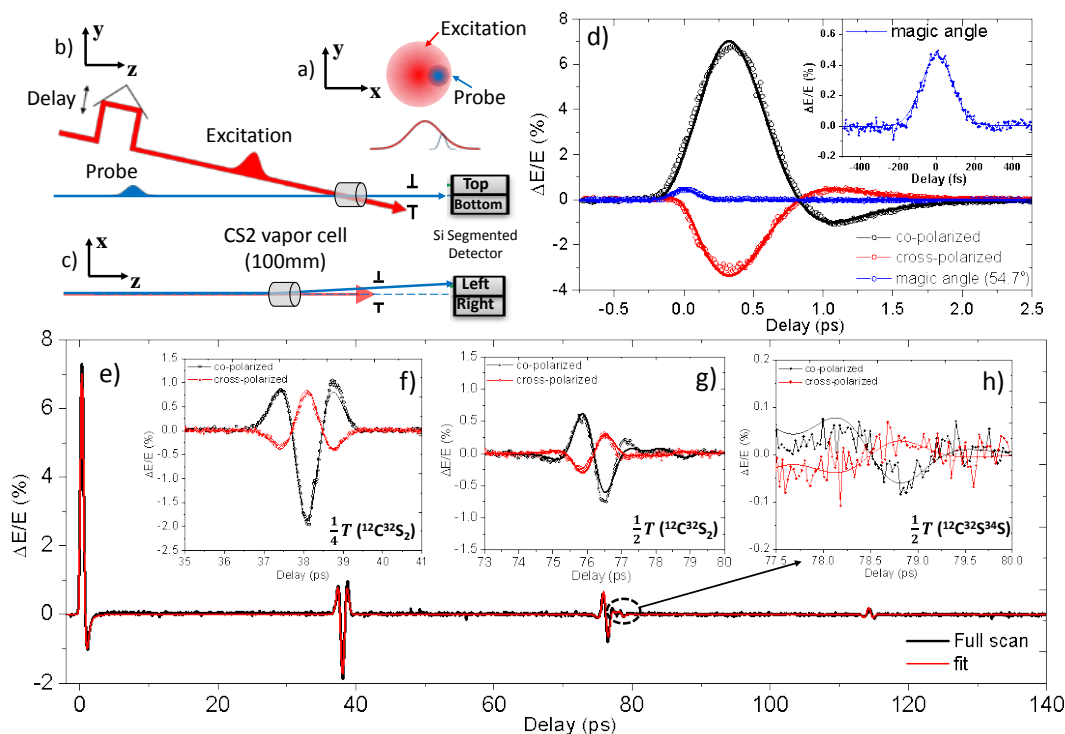
Fig. 1. (a-c) Excitation and probe overlap geometry in beam deflection measurement of gas-phase CS_2; (d) Polarization dependence of measured (circles) and fit (curves) signal at zero delay (inset shows enlarged magic angle measurement); (e) NLR response of CS_2 vapor with co-polarized excitation and probe measured up to 140ps. The inset show ¼ (f), ½ (g) revivals from $^{12}C^{32}S_2$ and ½ (h) revival from isotopologue $^{12}C^{32}S^{34}S$.

maximum at ~400 fs. The rotational response arises from the excitation induced net alignment of the molecular ensemble via Raman transitions. For polarization parallel ∥ and perpendicular ⊥ to the molecular axis of CS_2 with polarizability anisotropy $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, the excitation pulse creates birefringence when the molecules align towards the excitation polarization direction (i.e. < 400fs in Fig. 1d). Here the co- and cross-polarized probe will experience positive and negative Δn_{rot} respectively, following the reorientational symmetry $\Delta n_{rot,\perp} = -\Delta n_{rot,\parallel} / 2$. At the magic angle the rotational component is eliminated ($\Delta n_{rot} = 0$). This separation of Δn_{el} and Δn_{rot} enables the determination of the $Re[\gamma_s]$ through a relative measurement. With the well-known $\Delta\alpha$ (10.53×10^{-40} Fm^2) of CS_2 molecules from Ref. [5], we use the temporally delayed rotational response ($\Delta n_{rot} \propto N(\Delta\alpha)^2$) as a reference to measure the bound-electronic response ($\Delta n_{el} \propto NRe[\gamma_s]$) along with Δn_{rot} in a self-consistent measurement, where the measured magnitude of $\Delta n_{el}/\Delta n_{rot}$ is proportional to $Re[\gamma_s]/(\Delta\alpha)^2$ [1, 3]. Following the isotropic tensor symmetry $\Delta n_{el,\perp} = \Delta n_{el,\parallel} / 3$, we can fit Δn_{el} of the gas-phase CS_2 measurements for co-, cross- and magic-angle polarization data with $Re[\gamma_s]$(vapor) = $(1.8\pm0.4)\times10^{-61}$ C^{4}m^{4}J^{-3} (($1.5\pm0.3)\times10^{-36}$ esu), which is slightly smaller than (but within errors of) the $Re[\gamma_s]$(liquid) = $(2.2\pm0.5)\times10^{-61}$ C^{4}m^{4}J^{-3} (($1.8\pm0.4)\times10^{-36}$ esu) calculated considering local-field effects using $f^{(3)}\sim5.3$ and $n_{2,el} = (1.6\pm0.3)\times10^{-19}$ m^2/W from our liquid CS_2 measurements [2]. The NLR transients of CS_2 vapor are also measured with co-polarized beams for longer delays, where we observe the typical rotational revivals up to 3 quarter multiples of the revival period (T ~153 ps), as shown in Fig. 1e with fine structure at ¼T, ½T revivals in the insets, which correspond to a rotational constant of $B(^{12}C^{32}S_2) = 0.1093 \pm 0.0002$ cm^{-1}. Interestingly, the signal at ~79 ps turns out to be the first half revival from the isotopologue $^{12}C^{32}S^{34}S$ (Fig. 1h), which can be fit by assuming the natural abundance of ^{34}S (4.25%) and ^{32}S (95%) [6] with $B(^{12}C^{32}S^{34}S) = 0.1061 \pm 0.0008$ cm^{-1}.

3. Conclusion

The second hyperpolarizability of CS_2 is directly measured in gas-phase via the ultrafast nonlinear beam deflection method and is approximately equal to that measured in the liquid phase including local field effects. $Re[\gamma_s]$ of gas-phase molecules is of interest for comparison to theoretical models. By resolving the rotational response of $^{12}C^{32}S^{34}S$, beam deflection shows a potential application for isotope identification.

4. Reference

1.   Lin, C.H., et al., Physical Review A, 1976. **13**(2): p. 813-829.
2.   Reichert, M., et al., Optica, 2014. **1**(6): p. 436-445.
3.   Ferdinandus, M.R., et al., Optics Letters, 2013. **38**(18): p. 3518-3521.
4.   Armstrong, J.A., et al., Physical Review, 1962. **127**(6): p. 1918-1939.
5.   Bogaard, M.P., et al., Journal of the Chemical Society, 1978. **74**(0): p. 3008-3015.
6.   The Atomic Weights of the Elements: Review 2000 (IUPAC Technical Report), IUPAC. 2003. p. 21.