



Research paper

The sign of the polarizability anisotropy of polar molecules is obtained from the terahertz Kerr effect

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ABSTRACT

The terahertz Kerr effect (TKE) of polar molecular vapors is reported. The birefringence signal of fluorobenzene appears with opposite polarity compared to acetonitrile and water. This behavior is a hallmark of the opposite sign of a new molecular polarizability anisotropy $\Delta\alpha_{\text{TKE}} = \alpha_{zz} - (\alpha_{xx} + \alpha_{yy})/2$, with α_{zz} being the polarizability along the permanent dipole moment. As the excitation of the rotational states orients the permanent dipoles along the terahertz electric field, the orientation is translated into an optical birefringence proportional to $\Delta\alpha_{\text{TKE}}$. Thus, the sign of $\Delta\alpha_{\text{TKE}}$ is imprinted onto the TKE signal, providing novel insights into the polarizability tensor of water.

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1. Introduction

The spatial orientation or alignment of molecules can boost the yield of many physical and chemical processes such as photo-induced chemical reactions [1,2], high harmonic generation [3,4] and surface scattering phenomena [5,6,7]. Typically, the molecular orientation/alignment is achieved by applying an external DC electric field [8] or intense optical pulse [9] or the combination of both fields [10] to the molecular ensemble. Recently, Nelson and coworkers demonstrated a novel approach in which the field-free molecular arrangement is achieved through the resonant excitation of the rotational degrees of freedom of dipolar molecules with intense terahertz (THz) electric fields [11,12].

In this approach, a time (t)-dependent THz electric field $\mathbf{E}(t)$ exerts a torque $\boldsymbol{\mu} \times \mathbf{E}$ by direct coupling to the permanent molecular dipole moment $\boldsymbol{\mu}(t)$ with constant modulus μ , thereby orienting the molecular dipoles along the direction of \mathbf{E} . The associated interaction energy is given by $V_{\text{perm}}(\theta) = -\boldsymbol{\mu} \cdot \mathbf{E} = -\mu|\mathbf{E}|\cos\theta$ where θ is the angle between \mathbf{E} and $\boldsymbol{\mu}$ [11]. This mechanism is, however, not operative for optical light fields because the molecules cannot follow the rapid field oscillations [9].

On the other hand, molecular alignment can be achieved by coupling to the transient electronic dipole moment $\boldsymbol{\alpha}(t)\mathbf{E}(t)$ that is induced by the applied electric field [13,14]. Here,

$\boldsymbol{\alpha} = \boldsymbol{\alpha}(\varphi, \theta, \psi)$ is the polarizability tensor of the molecule considered. It depends on the Euler angles φ , θ and ψ that determine the molecule's rotational degrees of freedom. Since hyperpolarizabilities are generally small, we neglect the induced electronic dipole moments beyond linear order in \mathbf{E} . Consequently, the coupling energy is given by $V_{\text{ind}}(\varphi, \theta, \psi) = -{}^t\mathbf{E}\boldsymbol{\alpha}(\varphi, \theta, \psi)\mathbf{E}/2$, where ${}^t\mathbf{E}$ denotes the transpose of \mathbf{E} . The resulting torque is proportional to $(\boldsymbol{\alpha}\mathbf{E}) \times \mathbf{E}$ which vanishes if $\boldsymbol{\alpha}$ is scalar. Therefore, this mechanism only occurs for molecules with anisotropic $\boldsymbol{\alpha}$. In the particular case of symmetric-top (ST) molecules, the coupling energy simplifies to $V_{\text{ind}}(\theta) = -\Delta\alpha_{\text{ST}}\mathbf{E}^2\cos^2\theta/2$, where the molecular polarizability anisotropy $\Delta\alpha_{\text{ST}} = \alpha_{\parallel} - \alpha_{\perp}$ is given by the difference of the electronic polarizabilities parallel and perpendicular to the symmetry axis of the molecule. For the V_{ind} -type interaction, the time-averaged torque on the molecules does not vanish because the squared electric field in V_{ind} results in the rectification of the rapidly varying light field [9]. As a result, molecules will be aligned with the axis of their largest polarizability parallel to the driving field polarization.

Note that the V_{perm} -coupling orients the molecular dipoles along the direction of the driving field, whereas the V_{ind} -coupling aligns the axis of the largest molecular polarizability along the \mathbf{E} -field polarization [11]. Therefore, a different angular distribution of an ensemble of polar molecules is generally formed via V_{perm} and V_{ind} . While V_{perm} depends only on the angle θ between electric field \mathbf{E} and permanent dipole moment $\boldsymbol{\mu}$, V_{ind} in general involves all three Euler angles. As a consequence, a molecular ensemble oriented through the V_{perm} interaction is potentially easier to characterize than the one aligned with the V_{ind} interaction.

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In this work, we make use of intense THz fields to excite the rotational degrees of freedom of vapors of selected dipolar molecules and measure the induced optical birefringence. We show that the latter signals scale linearly with a new polarizability anisotropy of the molecules; therefore, allowing us to determine the relative orientation of the permanent versus induced dipoles in the molecules.

2. Theoretical background

We first develop a simple model of the measured signal in our experiment. It directly leads us to a new version of the polarizability anisotropy. As schematically shown in Fig. 1a, an intense THz electric-field pulse, polarized along the z-axis excites a molecular vapor. The instantaneous amplitude of the molecular orientation at a subsequent time t is measured by an optical probe pulse that detects the refractive-index difference $\Delta n(t)$ between the directions parallel (z-axis) and perpendicular (x-axis) to the driving linearly polarized THz field (the THz Kerr effect, TKE) [15].

To relate Δn to the microscopic observables, we note that its value is proportional to $\langle \alpha_{zz} \rangle - \langle \alpha_{xx} \rangle = \langle \alpha_{zz} \rangle - \langle \alpha_{yy} \rangle$ where angular brackets denote the average over all molecules in the probing volume. The last equality holds because the molecular ensemble including the THz field exhibits rotational symmetry around the z-axis. It follows that Δn is proportional to $2\langle \alpha_{zz} \rangle - \langle \alpha_{xx} \rangle - \langle \alpha_{yy} \rangle$ which can be rewritten as

$$\Delta n \propto (3^t \mathbf{e}_z \underline{\alpha} \mathbf{e}_z - \text{Tr} \underline{\alpha}). \quad (1)$$

Here, \mathbf{e}_z is the unit vector along the z-axis, and $\text{Tr} \underline{\alpha}$ denotes the trace of the matrix $\underline{\alpha}$. The ensemble average in Eq. (1) can be evaluated by integrating $\underline{\alpha}(\varphi, \theta, \psi) f(\varphi, \theta, \psi, t)$ over all Euler angles where $f(\varphi, \theta, \psi, t)$ is the instantaneous molecular distribution function. The polarizability is determined by $\underline{\alpha}(\varphi, \theta, \psi) = {}^t \mathbf{R}(\varphi, \theta, \psi) \underline{\alpha}^0 \mathbf{R}(\varphi, \theta, \psi)$ where $\underline{\alpha}^0$ is the polarizability tensor of a molecule with its permanent dipole moment oriented along the z-axis ($\theta = 0$). The matrix $\mathbf{R}(\varphi, \theta, \psi)$ describes the rotation of the molecule into the (φ, θ, ψ) -configuration. It equals the product $\mathbf{R}_\psi \mathbf{R}_\theta \mathbf{R}_\varphi$ of three sequential rotations, according to the definition of the Euler angles.

In equilibrium, f is isotropic and, thus, a constant. Assuming that the ensemble interacts with the THz electric field through

V_{perm} , the distribution function becomes θ -dependent but remains independent of φ and ψ , that is, $f = f(\theta, t)$. Thus, the ensemble average of the polarizability can be expressed by

$$\langle \underline{\alpha} \rangle = \iiint d\cos\theta d\psi d\varphi f(\theta) \underline{\alpha}(\varphi, \theta, \psi) \quad (2)$$

Since the trace is invariant under rotations and since $\mathbf{R}_\varphi \mathbf{e}_z = \mathbf{e}_z$, the evaluation of Eqs. (1) and (2) is greatly simplified and yields

$$\Delta n(t) \propto \Delta \alpha_{\text{TKE}} \int d\cos\theta f(\theta, t) (\cos^2\theta - 1/3). \quad (3)$$

The prefactor is given by

$$\Delta \alpha_{\text{TKE}} = \alpha_{zz}^0 - \frac{\alpha_{xx}^0 + \alpha_{yy}^0}{2} \quad (4)$$

and equals the difference of the molecular electronic polarizability along the direction of the permanent dipole and the arithmetic mean perpendicular to it. Remarkably, this result is valid for any polarizability tensor $\underline{\alpha}^0$, even for the case of mutually different tensor elements. It is also independent of the rotation of the molecule about the direction of the permanent dipole moment (z-axis). In the following, we omit the superscript 0 in the polarizability for brevity.

Eq. (4) can be considered as an alternative definition of the polarizability anisotropy and is different from the polarizability anisotropy $\Delta \alpha_{\text{Raman}} = \mp [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} / \sqrt{2}$ as obtained from Raman-type measurements [16,17]. Therefore, TKE experiments on molecular vapors can provide new information on the polarizability tensor of the constituting molecules. Only in the special case of ST molecules do both $\Delta \alpha_{\text{TKE}}$ (Eq. (4)) and $\Delta \alpha_{\text{Raman}}$ reduce to $\Delta \alpha_{\text{ST}} = \alpha_{\parallel} - \alpha_{\perp}$.

3. Experimental details

A schematic of our experiment is shown by Fig. 1a. A gas jet of molecules at position B is excited by intense, linearly polarized THz pulses from a Lithium Niobate (LN) source with field strength exceeding 2 MV cm^{-1} . The resulting transient optical birefringence is sampled by a time-delayed optical pulse (pulse energy 2 nJ, duration 8 fs, center wavelength 800 nm) whose linear polarization before the sample is at 45° with respect to the direction of

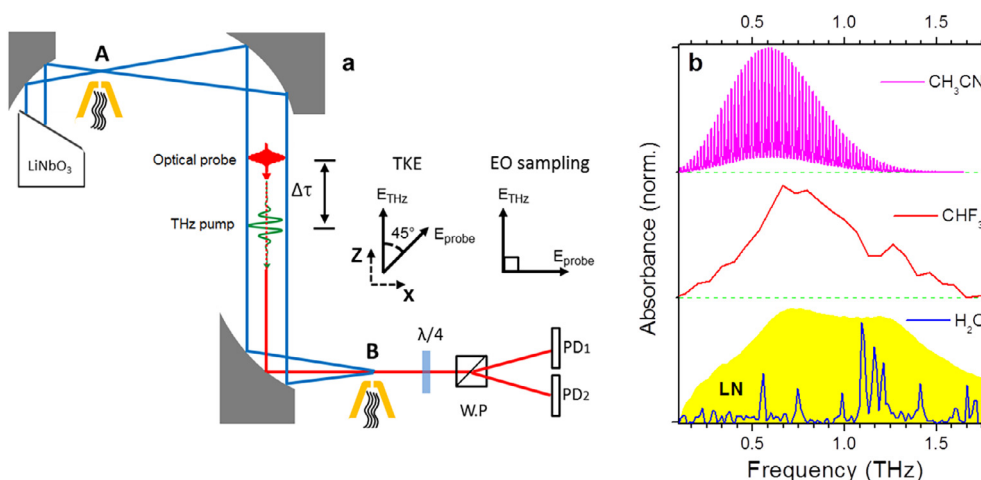


Fig. 1. (a) To measure THz-induced optical birefringence of gases, molecules of the sample gas are brought into the THz focus at position B by means of a nozzle. At this position, the transient birefringence induced by the THz pump pulse is measured by the collinearly propagating optical probe. For THz transmission measurements, the nozzle is placed at position A. After having traversed the sample gas, the transient THz electric field is sampled in an electrooptic (1 1 0)-oriented ZnTe crystal at position B. Abbreviations: $\lambda/4$: quarter waveplate, W.P.: Wollaston prism, PD: photodiode. (b) Red and blue solid lines show the measured THz absorption spectra of fluoroform and water vapor, respectively. The solid magenta line shows the simulated THz absorption spectrum of acetonitrile vapor [26,27]. The yellow area is the amplitude spectrum of the THz pump pulse from the lithium Niobate (LiNbO₃) source. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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