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The Nature of the Dielectric Response of Methanol Revealed by the Terahertz Kerr Effect

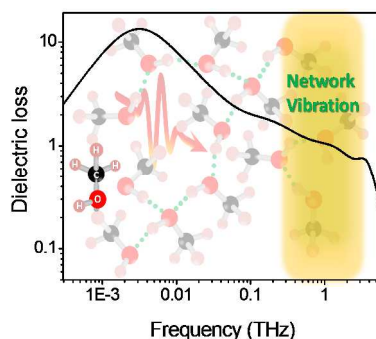
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ABSTRACT: The dielectric response of liquids in the terahertz (THz) and sub-THz frequency range arise from low-energy collective molecular motions, which are often strongly influenced by intermolecular interactions. To shed light on the microscopic origin of the THz dielectric response of the simplest alcohol, methanol, we resonantly excite this liquid with an intense THz electric-field pulse and monitor the relaxation of the induced optical birefringence. We find a unipolar THz-Kerr-effect signal which, in contrast to aprotic polar liquids, shows a weak coupling between the THz electric field and the permanent molecular dipole moment of the liquid. We assign this weak coupling to the restricted translational rather than rotational nature of the excited mode. Our approach opens a new avenue to the assignment of the dielectric spectrum of liquids to a microscopic origin.



Low-frequency molecular motions in liquids have significant impact on biological activity and solution phase chemistry.^{1,2} They affect many processes, such as solvation,³ energy transfer and proton transport.⁴ A macroscopic property reflecting (a part of) these collective and/or cooperative molecular motions is the dielectric susceptibility $\chi(\omega)$ (or, equivalently, the dielectric function) with frequencies $\omega/2\pi$ ranging from the gigahertz to the terahertz region. In the time domain, the dielectric susceptibility equals the temporal correlation function of the

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3 permanent dipoles and the dipoles induced by intermolecular interaction and/or collisions.⁵ The
4 latter induced dipole, depending on the nature of the intermolecular interactions, may even make
5 a strong contribution to $\chi(\omega)$.^{6,7,8,9} The oscillatory translational motions of the induced dipoles
6 occur at terahertz (THz, 1 THz \cong 33 cm⁻¹) frequencies and are believed to be a primary step to
7 the process of structural relaxation in liquids.^{10,11}

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15 To fully exploit the dielectric susceptibility $\chi(\omega)$ as a structural/dynamical probe of liquids, it is
16 important to determine the molecular motions that make the dominant contribution to $\chi(\omega)$ in a
17 given frequency range. In general, one may dissect $\chi(\omega)$ into (i) the rotational motions including
18 diffusive orientational (e.g. Debye process) and hindered rotational motions (librations) and
19 (ii) the translational motions including diffusive transport and restricted translational/vibrational
20 motions. For the assignment of spectral features of $\chi(\omega)$ to molecular motions, molecular
21 dynamics simulations are a powerful tool.^{6,7,8,9,10} Likewise, temperature-dependent
22 measurements of $\chi(\omega)$ ^{12,13} combined with suitable models may be conducted to gain insight into
23 the nature of intermolecular motions. However, the complexity of intermolecular interactions as
24 well as the large spectral overlap of the pertinent modes make the assignment to the underlying
25 dynamics challenging. Similar issues arise when the low-frequency intermolecular dynamics are
26 accessed by techniques such as Raman spectroscopy¹⁴ and neutron scattering.^{15,16}

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43 In addition to linear dielectric probing, time-resolved non-linear Raman spectroscopy may be
44 exploited to gain insight into the nature of the intermolecular motions¹⁷. However, the
45 implementation of non-linear Raman excitation schemes is often challenging because of the
46 small Raman-tensor elements of the interaction/collision-induced nuclear motions. In addition,
47 Raman spectroscopy and linear dielectric spectroscopy may address modes of different
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3 symmetry. Consequently, optical Raman probes are not a straightforward approach to the
4 assignment of the dielectric response to microscopic molecular motions.¹⁴
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8 Recently, a novel approach based on intense THz pulses has emerged in which these limitations
9 are, to some extent, relaxed. The reason is that the incident THz electric field is in resonance
10 with the rotational transitions of single molecules or the collective/cooperative low-frequency
11 motion of molecules, thereby enhancing the collected response.^{18,19,20,21} By implementing this
12 approach, we demonstrated that resonant excitation of rotational degrees of freedom of aprotic
13 polar liquids leads to a transient optical birefringence, induced by the THz electric-field torque
14 on the permanent dipole moment of the solvent molecules¹⁹ (called THz Kerr effect, TKE²²). We
15 observed an empirical hallmark of this effect¹⁹: a transient optical birefringence up to one order
16 of magnitude higher than obtained with high frequency, non-resonant, optical excitation (optical
17 Kerr effect, OKE).
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21 In this letter, we conduct the comparative “TKE versus OKE” (TvO) experiment in a protic polar
22 model liquid, namely methanol (CH₃OH), to explore the microscopic origin of the underlying
23 molecular motions in its low-frequency dielectric spectrum. In the TKE experiment we excite the
24 liquid with an intense electromagnetic pulse centered at ~1 THz and measure the resulting
25 optical birefringence by an optical probe pulse (see **Fig. 1a**). The birefringence induced by the
26 THz pump is found to be enhanced only weakly relative to that induced by an optical pump,
27 despite the sizeable dielectric susceptibility at the THz pump frequency. Comparison to the
28 birefringence induced by an optical pump, and the use of a simple model, allow us to determine
29 whether (restricted) translational or rotational molecular motions dominate the dielectric
30 response at the THz pump frequency.
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As shown in **Fig. 1b**, methanol has a structured dielectric spectrum that can be fit by three Debye-type contributions with relaxation times $\tau_{D_1} = 51.8$ ps, $\tau_{D_2} = 8.04$ ps and $\tau_{D_3} = 0.89$ ps and two Lorentzians centered at $\omega_{V_1}/2\pi = 1.7$ THz and $\omega_{V_2}/2\pi = 3.8$ THz.¹⁴ Microscopically, these fit functions may be ascribed, respectively, to the cooperative diffusive motion²³, single-molecule rotation,^{24,25} breaking-reforming dynamics of hydrogen bonds or the flipping of free OH groups,²⁴ fluctuation of the methyl group^{9,12} and the stretch vibration of the hydrogen bonding network.⁹

The liquid phase of methanol is described by the chain- and/or ring-like conformations with different numbers of molecules linked through H-bonds.²⁶ As a result, the collective dynamics associated with these local structures are complex (see **Fig. 1b**). However, as these dynamics occur in the THz frequency range, it is an ideal system for our proof-of-principle study.

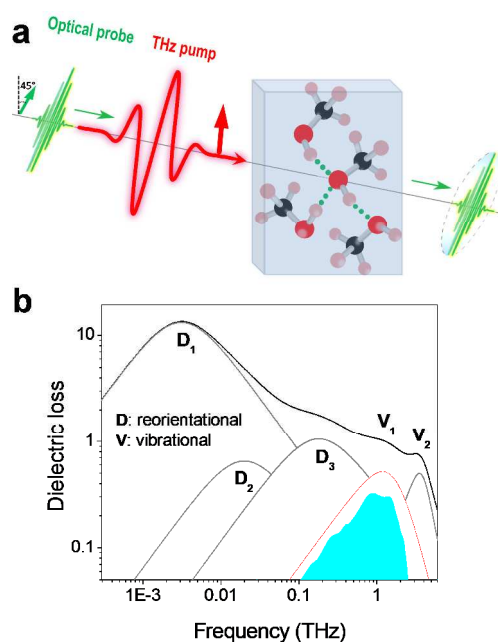
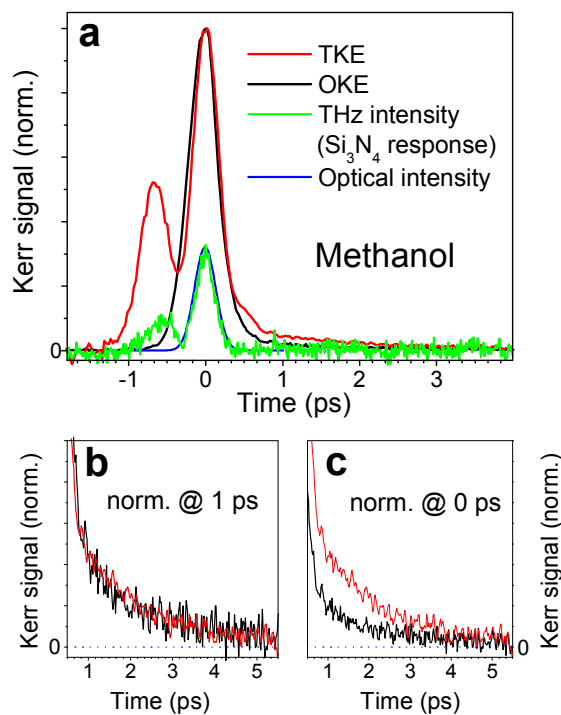


Figure 1 | THz Kerr effect of methanol. **a**, Upon propagation of an intense THz or optical pump pulse through methanol (CH₃OH), the linear polarization of a probe pulse becomes elliptically polarized. **b**, Dielectric loss spectrum of methanol (black line) is fit by three Debye functions (D₁, D₂, D₃) and two Lorentzians (V₁ and V₂). The amplitude spectrum of the THz pump pulse is indicated by the cyan area.

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3 In our experiment, an intense electromagnetic pump pulse centered at ~ 1 THz is focused on the
4 sample. The resulting transient optical anisotropy is measured by a temporally delayed probe
5 pulse (pulse energy 2 nJ, center wavelength 800 nm, duration 8 fs). To directly compare the
6 THz-induced anisotropy to that induced by optical excitation, we conduct the same measurement
7 but with the THz pulse replaced by an optical pump pulse. The instantaneous intensities of the
8 optical and the THz pump pulses have similar temporal shapes (see **Fig. 2a**). For the TKE and
9 the OKE measurements, methanol is kept in a cell for which the choice of window materials is
10 important. The selected window



46 **Figure 2 | Transient optical birefringence of methanol following THz and optical excitation. a**, TKE
47 (red line) and OKE (black line) signals of methanol. Signals are normalized to the initial peak signal
48 where the instantaneous electronic contribution is expected to dominate the birefringence signal. The
49 instantaneous squared THz electric field (measured as the TKE response of a 150 nm thick silicon nitride
50 membrane, Si₃N₄) and the optical pump pulse are shown as the green and blue lines, respectively. **b**, The
51 data in panel **a** are normalized to the signal amplitude at a delay of ~ 1 ps. **c**), same as panel **a** but zooms
52 in the relaxation tails of the OKE and TKE signals.

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3 (a 150 nm thick Si₃N₄ membrane) is transparent at both THz and optical frequencies, optically
4 isotropic and has a small as well as short-lived nonlinear THz response.²⁷ To ensure that the
5 accumulation of the pump heat from the 1 kHz train of pump pulses does not influence the TKE
6 results, we also performed the TKE experiments in a flow cell. We found no difference between
7 the two cells in the dynamics and the amplitudes of the signals. The sample liquid, methanol
8 (99.9%), was purchased from Sigma Aldrich and used as received.
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12 The measured transient birefringence of methanol following THz and optical excitation is shown
13 in **Fig. 2a**. The measured signals share two common features: (i) a sharp initial rise with a shape
14 similar to the squared THz pump field $E^2(t)$ and optical intensity envelope $I(t)$, respectively,
15 followed by (ii) a slower decay on a picosecond time scale. Note that the TKE and OKE signals
16 of methanol are unipolar, i.e. both features have the same sign. Feature (i) is assigned to the
17 instantaneous electronic response of methanol.²² The slower feature (ii) is assigned to the
18 relaxation of the molecular nuclear degrees of freedom. Similar unipolar TKE signals are also
19 observed in a series of *n*-alcohols (see **Fig. S1**).
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37 An important result is achieved by normalizing the OKE and TKE signals at time $t \approx 1$ ps, at
38 which pump and probe pulses have no overlap anymore and the electronic response has totally
39 decayed. As shown in **Fig. 2b**, at longer delay times, identical relaxation is observed for both
40 signals. This finding may imply that the relaxation of identical processes occurs after the optical
41 and the THz excitation. The induced optical birefringence in methanol decays with an average
42 time of ~ 1 ps, in line with previous OKE studies.^{17,28}
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52 Further insight is obtained by normalizing the OKE and TKE signals of methanol to the peaks of
53 their electronic response at $t = 0$. As the optical and THz pulses have comparable duration, this
54 procedure is tantamount to normalizing the signals to the pump intensity. As shown in **Fig. 2a**
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3 and \mathbf{c} , once pump-probe overlap is negligible ($t > 1$ ps), the TKE signal shows a slightly (i.e. a
4 factor of ~ 2) larger amplitude. The enhancement of the TvO signal is expected for polar
5 molecules with positive polarizability anisotropy.²⁹
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10 These findings are remarkable because an identical birefringence relaxation is observed in the
11 OKE and the TKE process, despite the difference in their excitation mechanism. (i) The optical
12 pump pulse (OKE) drives the low-frequency modes of the liquid by an off-resonant Raman
13 process, while (ii) the THz pump pulse (TKE) drives the infrared (THz)-active modes of
14 methanol, thereby inducing optical birefringence through a resonant excitation.¹⁹ In particular,
15 since methanol is highly polar³⁰, one expects that a strong optical anisotropy results from the
16 coupling of the THz electric field, $E(\omega)$ and the transition dipole moment of the liquid at the
17 pump frequency. However, the TKE signal of methanol exhibits an enhancement of only ~ 2
18 relative to the OKE signal, in contrast to aprotic polar liquids such as acetonitrile and DMSO,
19 where the TKE signal was almost one order of magnitude larger than the OKE signal.¹⁹
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34 To interpret this result, we note that in the Kerr-effect, the transient optical birefringence is
35 assumed to arise predominantly from the molecular rotational degrees of freedom. Then, the
36 transient birefringence scales with the difference^{31,32}
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$$\Delta n(t) \propto \Delta\alpha \int du f(u,t) P_2(u) \quad (1)$$

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43 of the liquid's optical refractive index perpendicular and parallel to the driving field \mathbf{E} . Here, $\Delta\alpha$
44 is the molecular polarizability anisotropy, $u = \cos \theta$ is the cosine of the angle between \mathbf{E} and the
45 molecular axis, $f(u,t)$ is its instantaneous distribution and $P_2(u)$ is $(3u^2 - 1)/2$.
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3 Recently, we developed a simple model¹⁹ for the dynamics of $f(u, t)$ which allows us to
4 estimate the contributions due to the torque of the pump field on the permanent and on the pump-
5 field-induced electronic dipoles to the transient optical birefringence signal by the relation
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$$\Delta n(t) \propto R_2 * [E \cdot (N\Delta\alpha E + 3\chi^{\text{ori}} * E)]. \quad (2)$$

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11 Here, $E(t)$ is the amplitude of the linearly polarized optical or THz pump field and N is the
12 number of molecules per volume. In the convolution $(\chi^{\text{ori}} * E)(t) = \int dt' \chi^{\text{ori}}(t - t')E(t')$, the
13 function χ^{ori} is the contribution of the orientational molecular motion to the total dielectric
14 susceptibility of the liquid.
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23 Equation (2) can be understood as follows: the first field interaction generates an effective
24 electronic ($N\Delta\alpha E$) and orientational polarization ($3\chi^{\text{ori}} * E$) which, in turn, serves as a handle
25 for the second field interaction to generate a P_2 -type rotational anisotropy and, thus, optical
26 birefringence. The decay of this anisotropy is captured by the response function $R_2(t)$. It is
27 noteworthy that the second interaction with the pump field converts the dielectric response into
28 the Raman-type response function $R_2(t)$.
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38 Using Eq. (2), we can directly calculate the enhancement of the TvO signal. To calculate the
39 birefringence induced by an optical pump field $E(t)$, the total polarization is given by $N\Delta\alpha E$
40 because the orientational polarization is negligible at optical frequencies, $\chi^{\text{ori}} * E = 0$. Note that
41 the collision/interaction-induced contribution to the total polarizability, to the best of our
42 knowledge, cannot be determined experimentally. Thus, we here use the single-molecule
43 polarizability anisotropy of methanol ($\Delta\alpha = 2.2 \text{ \AA}^3$)³³. To calculate the THz-induced
44 birefringence as a function of the THz pump frequency ω_{THz} , we assume a narrowband THz
45 pulse centered at ω_{THz} . This procedure requires knowledge on χ^{ori} , which contains contributions
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from all infrared (THz)-active rotational motions, including hindered rotations (libration), diffusive orientational motion of single molecules as well as molecular clusters, but not the (restricted) translational motion. Therefore, it is vital to reliably decompose the total dielectric susceptibility χ into its contributions related to the rotational (χ^{ori}) and translational/vibrational (χ^{trans}) motions, i.e. $\chi = \chi^{\text{ori}} + \chi^{\text{trans}}$.

However, this decomposition cannot be implemented solely based on the dielectric spectrum of the liquid under consideration. Typically, the dielectric susceptibility $\chi(\omega)$ is fit by appropriate functions and accordingly interpreted, although the soundness of the assigned nature to the fit functions and even the uniqueness of the fit cannot be verified independently. An approach by which the symmetry and the nature of the intermolecular motions can be determined is polarization-selective Raman scattering.¹⁷ In this approach, the Raman response may be decomposed into the isotropic (translational) and anisotropic (rotational) contributions. However, as mentioned above a general procedure by which the Raman response of a liquid can be converted to the dielectric response does not exist, in particular for aprotic polar liquids.^{14,34}

Moreover, the weak Raman response of many

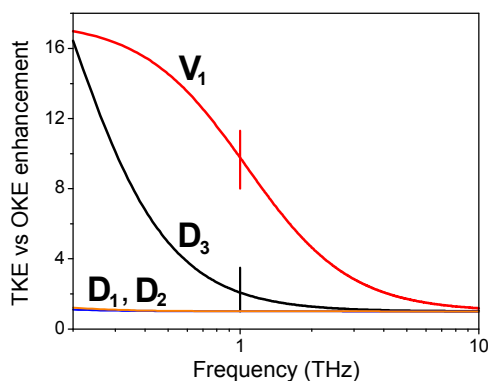


Figure 3 | Predicted enhancement of TKE vs OKE signal. Enhancement of the TKE versus OKE signal is plotted against the frequency of the excitation pulse. The black and red curves show the expected enhancement for the fastest Debye term D_3 and the slowest vibration V_1 , respectively. The contribution of the process D_1 and D_2 to the enhancement is small, the blue and orange lines, respectively. Small bars mark the peak frequency of the excitation THz pulse.

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3 liquids including water and methanol makes the implementation of the latter method challenging.
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5 Therefore, as motivated by Eq. (2), we suggest to use the comparative TvO procedure to assign
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7 features of $\chi(\omega)$ to translational or rotational molecular motions.
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10 To this end, we calculate the enhancement of its TvO signal as function of the excitation
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12 frequency for two scenarios. First, we assume that the dielectric spectrum of methanol up to ~ 3
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14 THz is fully due to the orientational degrees of freedom and can be expressed by Debye
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16 processes. As shown in **Fig. 1b**, the THz pump spectrum overlaps almost perfectly with the
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18 mode V_1 . In our first scenario this feature is assumed to arise from a Debye process with $\tau_D \approx$
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20 0.3 ps. As shown by the red curve in **Fig. 3**, the enhancement factor of the TvO signal of the V_1
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22 mode is ~ 10 , which strongly exceeds the value obtained from the experiment. As a second
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24 scenario, we assume that the V_1 mode has no contribution to the TKE signal and only consider
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26 the partial overlap of the THz driving field and the Debye process D_3 process of methanol.
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28 Interestingly, as shown by the black curve in **Fig. 3**, the excitation of the process D_3 causes a
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30 small enhancement of ~ 2 , which agrees well with the experimental result. Each of the other two
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32 Debye contributions D_1 and D_2 gives rise to a much smaller enhancement of the TKE signal.
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39 The previous scenarios lead to an interesting conclusion regarding the nature of the excited
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41 modes and the assignment of the molecular motion associated with the relaxation tail of the
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43 dynamic Kerr response of methanol. (i) As the D_3 process reproduces the expected amplitude
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45 enhancement of the TvO signal, the relaxation tail with a time constant of ~ 1 ps (see **Fig. 2**)
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47 likely originates from the reorientational motion of single molecules and/or small supramolecular
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49 structures. (ii) The large difference between the enhancement factors of the TvO signal as
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51 obtained from the model (factor of ~ 10) and from the experiment (factor of ~ 2) strongly suggests
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53 that the excited mode V_1 is mainly isotropic. Based on our model, the polarizability $P = \chi * E$
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3 can only be converted to an anisotropic distribution of the permanent dipoles if the applied THz
4 electric field excites the molecular rotational degrees of freedom. Conversely, for a translational
5 motion one can envisage that even a resonant excitation cannot alter the isotropic rotational state
6 of the liquid into an anisotropic state.
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12 We thus conclude that the dielectric spectrum of methanol around ~ 1 THz arises predominantly
13 from translations/vibrations (see above). Moreover, our results indicate a weak intermolecular
14 coupling between the excited vibrational mode and the observed reorientational relaxation in
15 methanol. Otherwise, through the coupling of the intermolecular modes, the TKE signal would
16 also gain enhanced amplitude, as was recently invoked for aprotic polar liquids.¹⁹ The latter
17 assignment of the V_1 mode (see **Fig. 1b**) to a symmetric vibration is consistent with previous
18 suggestions from temperature dependent dielectric-relaxation measurements, i.e. $\epsilon(\omega, T)$.^{12,13}
19 Note that our results confirm this assignment without adopting any model for describing $\epsilon(\omega, T)$.
20 Furthermore, our result is in line with molecular-dynamics (MD) simulations of methanol in
21 which a strong contribution of the restricted translational motion in the ~ 1 -2 THz spectral region
22 is predicted.^{6,7,8,9,10}
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39 Our results suggest the following excitation scenarios by which the observed reorientational
40 dynamics of methanol, driven by the THz electric fields, can be explained (see the schematic of
41 **Fig. 4**). Despite resonant excitation of the low-frequency infrared (THz)-active motions of
42 methanol at ~ 1 THz, the amplitude of the TKE signal shows only a small amplitude
43 enhancement relative to the off-resonant OKE signal. This resonant excitation is unlikely to
44 induce optical anisotropy in methanol, because of the symmetric (restricted) translational nature
45 of the excited mode. However, it is more likely that the small spectral overlap of the THz pump
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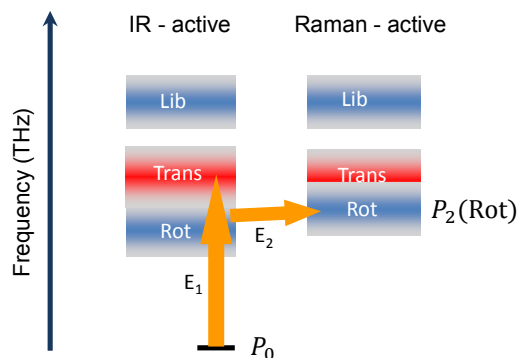


Figure 4 | Mechanism of the THz-pump-driven reorientational dynamics in methanol. Upon THz excitation, a polarization $P_1 = \chi * E_1$ can be induced through the IR (THz)-active modes of methanol, including rotational (Rot), restricted translational (Trans) and librational (Lib) motions. The second field interaction (E_2) converts the induced polarization into an optical anisotropy (Raman-active modes). Note that to detect the latter anisotropy as optical birefringence in the TKE signal, the orientational distribution of the molecules (i.e. a P_2 type distribution, see Eq. (1)) needs to be changed. Therefore, not even a resonant excitation of the (restricted) translational motion of molecules is expected to induce orientational anisotropy in methanol.

reorientational motions of methanol is sufficient to induce rotational anisotropic dynamics in methanol.

Higher spectral resolution for characterizing the low-frequency dynamics in liquids can be achieved by a two-dimensional TKE experiment.²¹ In addition, the development of a polarization-selective¹⁷ TKE spectroscopy will reveal further insight into the nature of intermolecular modes and their coupling. Finally, as the monohydroxyl alcohols are known as exceptional glass formers,³⁵ temperature-dependent studies of the TvO signal of these liquids may enable us to further test the assignment of dielectric spectral features to α relaxation, excess-wing or β relaxation and high-frequency γ relaxation.^{36,37,38,39} This approach may also provide a better understanding of the nature of the boson peak in these liquids.^{12,13}

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Supporting Information.

The THz Kerr effect signals of methanol, ethanol, propanol, butanol, pentanol and hexanol.

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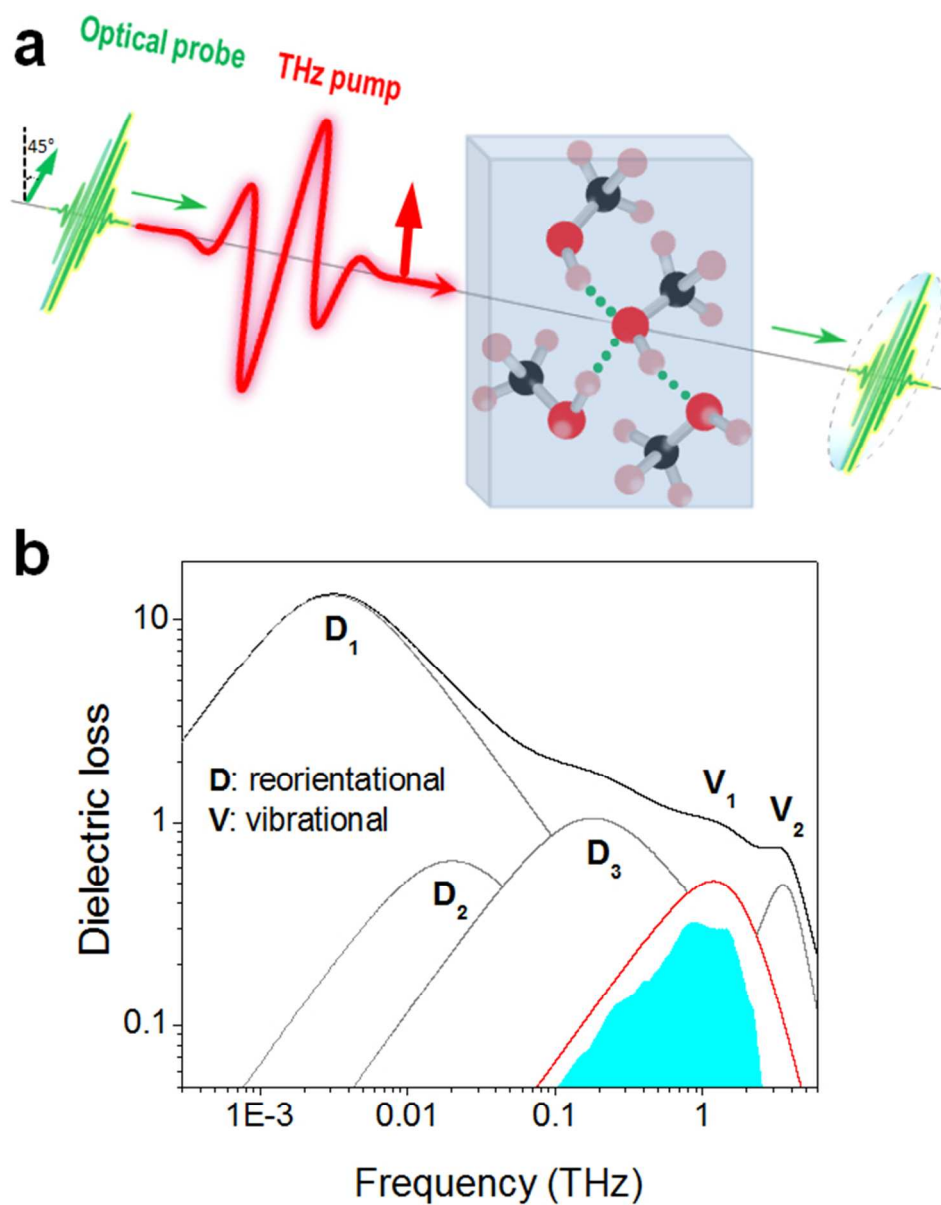
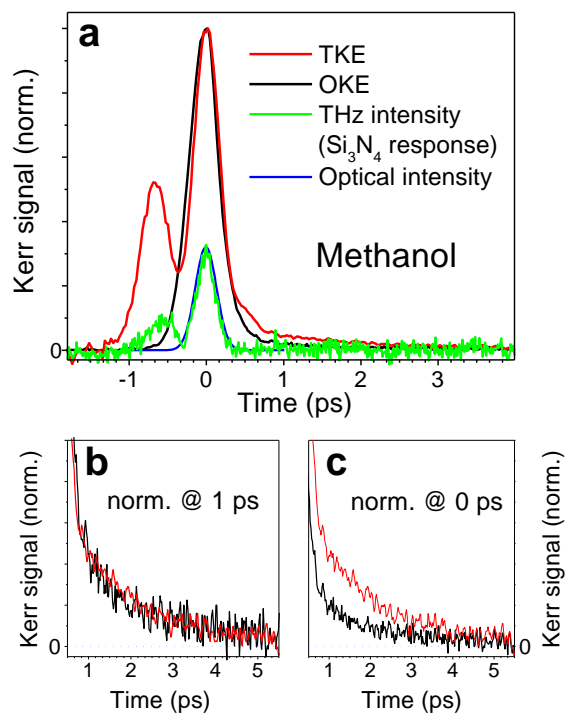
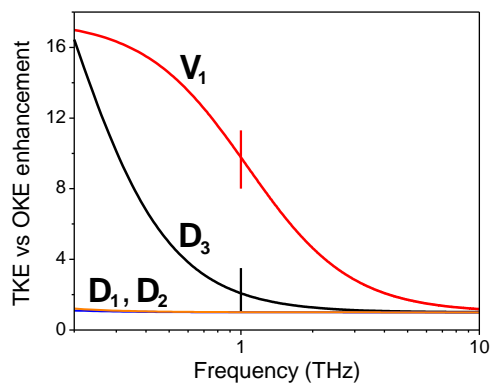


Figure 1 | THz Kerr effect of methanol. a, Upon propagation of an intense THz or optical pump pulse through methanol (CH₃OH), the linear polarization of a probe pulse becomes elliptically polarized. b, Dielectric loss spectrum of methanol (black line) is fit by three Debye functions (D₁, D₂, D₃) and two Lorentzians (V₁ and V₂). The amplitude spectrum of the THz pump pulse is indicated by the cyan area.

175x222mm (96 x 96 DPI)





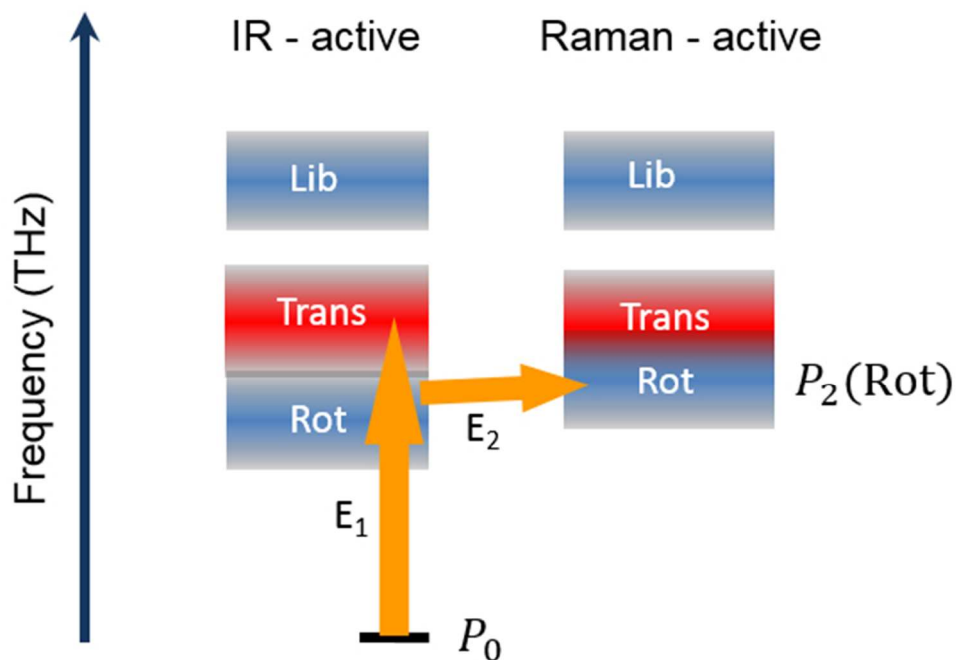


Figure 4 | Mechanism of the THz pump-driven reorientational dynamics in methanol. Upon THz excitation a polarization $P_1 = \chi \cdot E_1$ can be induced in the IR (THz) – active modes of methanol, including rotational (Rot), restricted translational (Trans) and librational (Lib) motions. The second field interaction (E_2) converts the induced polarization into an optical anisotropy (Raman – active modes). However, to resolve the latter anisotropy in a TKE signal, the orientational distribution of the molecules (i.e. a P_2 type distribution, see text) should be changed. Thereby, even a resonant excitation of the (restricted) translational motion of molecules does not induce orientational anisotropy in methanol.

125x88mm (120 x 120 DPI)