

# A new dynamic probe of electric forces between molecules

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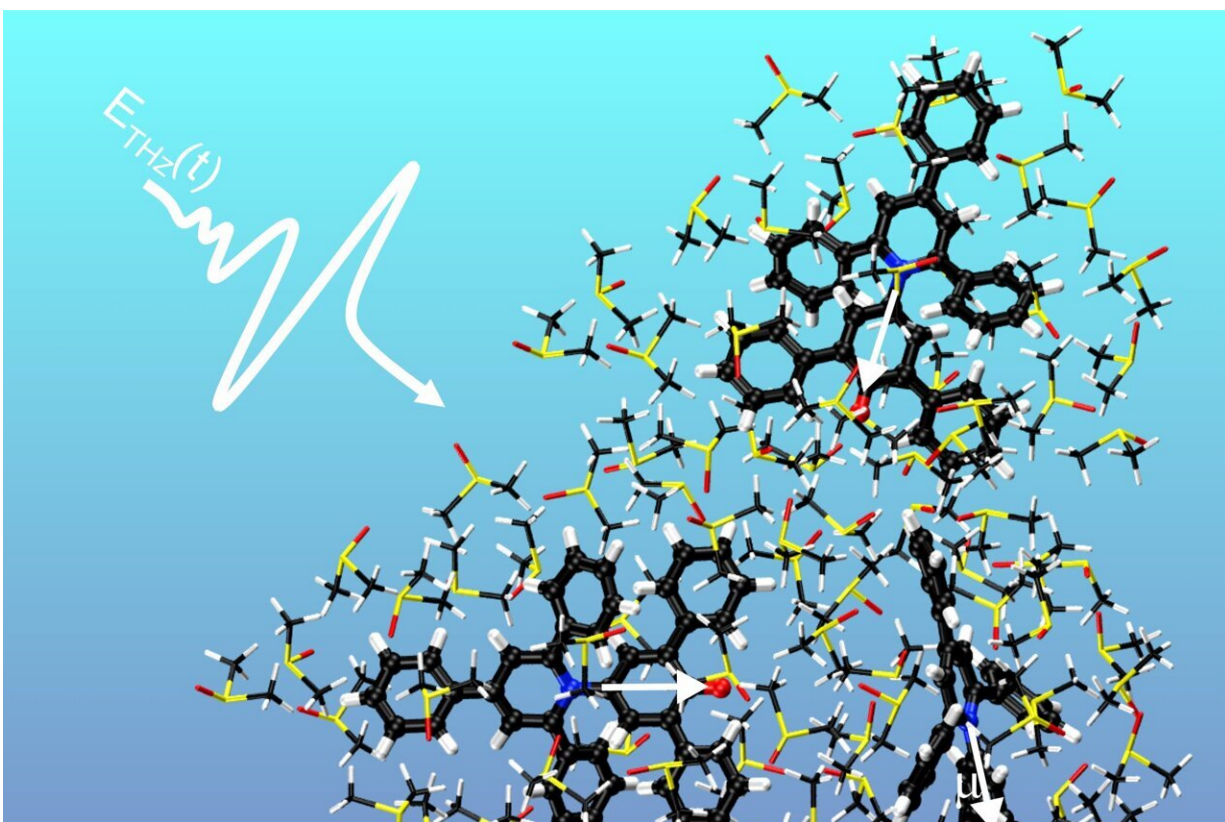


Fig. 1. Molecular structure of the dye betaine 30 (dark contours) in the solvent dimethyl-sulfoxide (DMSO). The disordered dye molecules possess a permanent electric dipole moment along their longitudinal axis (white arrows). The interaction with the time-dependent THz electric field  $E_{\text{THz}}(t)$  changes the energy of the ground state  $S_0$  and the first excited state  $S_1$  of the molecules (level scheme bottom left) and, concomitantly, the frequency position of optical absorption. This spectral shift is mapped in real-time by an ultrashort probe pulse  $I_{\text{probe}}(t)$ . The sign and the amount of the spectral shift (spectra bottom right)

depend on the spatial projection of the local THz electric field onto the molecular dipole direction. The experiment provides the temporal evolution of the absorption spectrum averaged over all dipole orientations. Credit: MBI B. Fingerhut/J. Zhang

Molecules in water and other polar media are subject to strong electric forces. Such forces originate from their liquid environment, which at ambient temperature undergoes ultrafast structural fluctuations. A new method maps the optical absorption of molecules in the electric field of an ultrashort terahertz pulse to determine the strength and dynamics of electric interactions.

The spectral shift of optical transitions in an external electric field, the so-called Stark effect, is a fundamental quantum effect in light-matter interaction, giving information on atomic and molecular properties. So far, the Stark effect has mainly been studied under stationary conditions to elucidate the time-averaged behavior of a single quantum system and/or an ensemble. In contrast, time-resolved measurements allow for observing transient properties and give insight in processes on an atomic scale.

Scientists from Max Born Institute in Berlin und Ludwig-Maximilians-Universität in Munich now have used [strong electric fields](#) in the terahertz frequency range ( $1 \text{ THz} = 10^{12} \text{ Hz}$ ) to modify the optical [absorption](#) of dye molecules in liquid solution and follow the ultrafast absorption changes in time.

They report in *The Journal of Physical Chemistry Letters* that interaction with a THz pulse of a 1-ps duration ( $1 \text{ ps} = 10^{-12} \text{ s}$ ) broadens the electronic absorption spectrum of the molecules substantially. This transient effect provides quantitative insight in the coupling of the

molecules to the external electric field and, at the same time, allows for calibrating the electric field from the solvent. A detailed theoretical analysis shows that the spectral shape of the absorption band is governed by the fluctuating electric forces in the liquid.

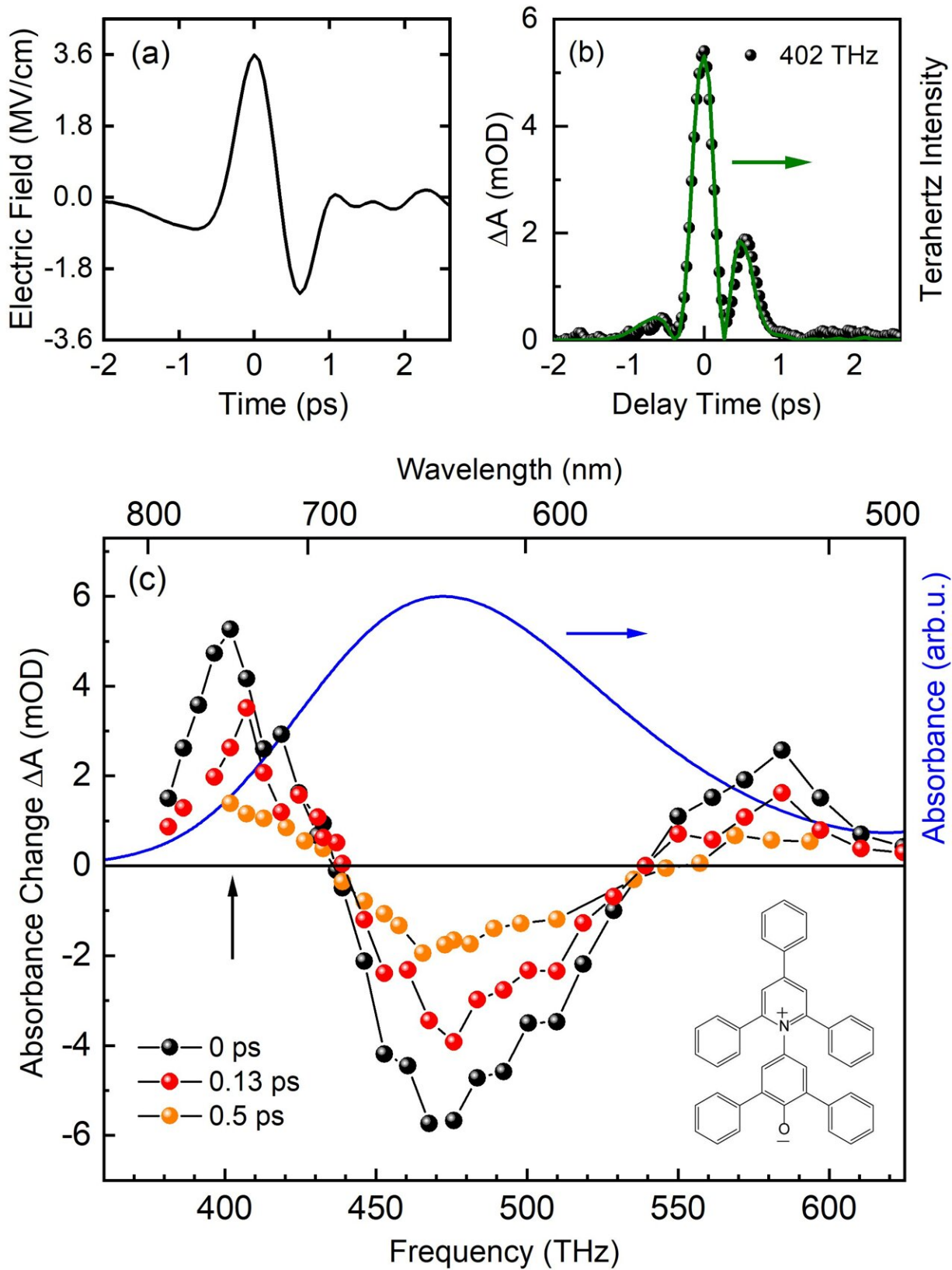


Fig. 2. (a) Time dependence of the THz electric field with a maximum amplitude of 3.6 MV/cm at the location of the dye molecules. (b) Time dependent THz intensity (solid line), corresponding to the absolute square of the THz field in panel (a). The symbols give the absorption change of the dye solution at a frequency of 402 THz (wavelength 746 nm, black arrow in panel (c)) as a function of time delay between the maximum of the THz electric field and the probe pulse. The absorption change follows the THz intensity in time. (c) Stationary absorption spectrum of betaine 30 in DMSO (blue solid line, no THz field) and transient absorption spectra for different delay times (symbols). The change of absorption, i.e., the difference of absorbance with and without THz field, is plotted as a function of probe frequency (bottom abscissa scale) or wavelength (upper abscissa scale). The shape of the transient spectra reflects a spectral broadening with an absorption decrease in the center and absorption increases on the wings of the stationary spectrum. The molecular structure of betaine 30 is shown as an inset. Credit: *The Journal of Physical Chemistry Letters* (2023). DOI: 10.1021/acs.jpcclett.3c01079

In the experiments, an ultrashort THz pulse interacts with a solution of the dye betaine-30 (Fig. 1). The THz electric field acting on the molecules is enhanced with the help of a metallic antenna structure and reaches a maximum value of 3.6 megavolts/cm (MV/cm, Fig. 2a), corresponding to approximately one third of the fluctuating field from the solvent. The momentary change of molecular absorption is monitored by probe pulses of a 100-fs duration. The [time evolution](#) is recorded by changing the delay between the two pulses.

The time evolution of the THz electric field is shown in Fig. 2a, the time dependent THz intensity in Fig. 2b (solid line). In Fig. 2c, the absorption change of the dye solution (symbols) is plotted as a function of frequency (bottom abscissa scale) and wavelength (upper abscissa scale). The solid blue line represents the stationary absorption spectrum in absence of a THz field. The transient absorption decrease in the center

of the stationary spectrum and the absorption increase on the low- and high-frequency wings correspond to a transient spectral broadening, induced by the THz electric field. In time, this broadening follows the THz intensity (Fig. 2b, symbols), while a contribution of the solvent to the absorption changes is absent. On the ultrashort time scale of the measurement, the solvent is structurally "frozen."

In the [liquid solution](#), there exists a disordered ensemble of dye molecules, each molecule possessing a permanent electric dipole moment (Fig. 1). The interaction of such dipoles with the THz [electric field](#) shifts the electronic transition between the ground state  $S_0$  and the first excited state  $S_1$  in frequency (level scheme in Fig. 1). The interaction strength and, thus, the sign and amount of spectral shift are determined by the projection of the THz field onto the direction of molecular dipole moment. As a result, the transient spectra in Fig. 2c reflect the orientally averaged behavior of the dye [molecules](#). A quantitative analysis of the spectral broadening gives the electric coupling strengths and allows for an experimental calibration of the electric fields in the solution. Beyond this basic insight, the ultrafast and fully reversible character of the field-induced absorption changes may lead to applications in optical switches and modulators.

**More information:** Poonam Singh et al, Transient Terahertz Stark Effect: A Dynamic Probe of Electric Interactions in Polar Liquids, *The Journal of Physical Chemistry Letters* (2023). [DOI: 10.1021/acs.jpcllett.3c01079](#)

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