Far-infrared properties of DAST

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Using terahertz time-domain spectroscopy, we have measured the index of refraction and the absorption coefficient of the organic ionic salt 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST). This promising organic electro-optic material exhibits strong absorption and dispersion for frequencies above 1 THz at both room temperature and 83 K. No reduction in the absorption strength is observed when DAST is cooled, suggesting a single-phonon origin of the resonances. A simple vibration of the anion and cation of the salt is suggested as the origin of the exceptionally strong far-infrared absorption and the high-frequency electro-optic properties of DAST.

The past decade has seen increasing applications of tailored organic materials in nonlinear optics. Most organic molecules with high hyperpolarizability will crystallize in centrosymmetric crystals as a result of the strong dipole–dipole interaction and will consequently not exhibit second-order nonlinearity \( \chi^{(2)} \). However, by incorporating highly nonlinear molecules as cations in organic salts one can, depending on the anion, obtain noncentrosymmetric crystals with large macroscopic second-order optical nonlinearity. One of the best examples is the organic salt 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST), whose chemical structure is shown in Fig. 1. Large DAST crystals of good optical quality can be grown, and the combination of low dielectric constant and high nonlinearity makes DAST crystals promising candidates for high-speed modulation and frequency mixing applications, including generation and detection of terahertz (THz) radiation. The most recent application of DAST crystals has been for high-frequency electro-optic modulation, detection, and generation of THz radiation, either through difference-frequency generation (DFG) mixing of two simultaneously oscillating lines from an electronically tuned Ti:Al\(_2\)O\(_3\) laser or by use of femtosecond optical pulses. The modulation frequencies are approaching 0.1 THz, and the frequencies of the difference-frequency generated THz beams are well into the THz regime (\( \nu = 1.4 \) THz); knowledge of the linear optical properties of DAST becomes important for phase-matching and efficiency considerations. In this Letter we report the index of refraction and the absorption coefficient of DAST in the range from 0 to 3 THz (0 to \( 90 \) cm\(^{-1}\)). The data were obtained by THz time-domain spectroscopy. Only limited information is available on the properties of molecular crystals in the far-infrared (THz) spectral region, and, in addition to practical applications, the far-infrared properties of DAST provide an illustrative example of the very strong and characteristic interaction between far-infrared radiation and molecular crystals.

We use a standard THz spectrometer with an additional focus added that allows us to investigate small samples (minimum sample diameter, \( \sim 0.5 \) mm). To ensure linear polarization of the THz pulse, a wire grid polarizer is inserted between the THz emitter and the sample. The ratio of the detected vertical-to-horizontal field amplitude is smaller than 1:250. The present setup can generate and detect THz radiation with a high signal-to-noise ratio (S/N) from 0.1 to 4 THz. The samples are mounted in a flow cryostat equipped with high-resistivity silicon windows. The temperature can be controlled to better than 0.1 K from 78 to 400 K. The temperature is measured close to the sample with a calibrated silicon diode.

The DAST crystals examined were high-quality crystals grown by controlled temperature lowering of a saturated methanol solution containing small seed crystals. The crystalline quality was controlled and confirmed in a polarization microscope. The two crystals used had thicknesses of 465 ± 3 and 435 ± 3 \( \mu \)m, with the crystallographic \( c \) axis perpendicular to the flat surface of the crystals. The \( c \) axis and the

Fig. 1. Chemical structure of DAST.
dielectric \( z(3) \) axis coincided, and we report the optical properties of the \( x(1) \) and \( y(2) \) axes, corresponding to the complex index of refraction \( n_m = n_m + i(\alpha_m c/2\omega) \), where \( m \) is equal 1 or 2. The \( x(1) \) axis of the dielectric tensor nearly coincided with the crystallographic \( a \) axis, and the \( y(1) \) axis coincided with the \( b \) axis of the crystals.

Figures 2 and 3 show the index of refraction and the absorption coefficient obtained by rotation of the crystal in the linearly polarized THz beam. In each figure, the index and absorption are shown both at room temperature and at 83 K. Good agreement between the index and absorption are shown both at room temperature and at LN\(_2 \) temperature, except for the peak value of the absorption coefficient. The maximum absorption coefficient measurable can be obtained from the S/N of the THz time-domain spectrometer. Assuming that the crystal absorbs all the THz radiation at a given frequency, the spectral amplitude at this frequency is given by the standard expression for a Lorentzian oscillator.

Good agreement was obtained both at room temperature and at 83 K. From a simple estimate of the transverse optical mode frequency, \( \omega_{TO} = N e^2(\varepsilon_o + 2)/9 \mu \varepsilon_0 (\varepsilon_{de} - \varepsilon_o) \), we obtained room-temperature resonance frequencies of \( \omega_{TO}^2/2\pi = 2.28, 1.13, 1.50 \) THz, where \( i = 1, 2, 3 \), corresponding to the main axis of the dielectric tensor. Density \( N \) was obtained from the volume of the unit cell, \( V = 2.098 \) nm\(^3\) with four DAST molecules per unit cell; \( \mu \) is the reduced mass of the anion–cation pair and is equal to 100 u. The estimates include the full unscreened ionic charge and are in qualitative agreement with the observed resonances in Figs. 2 and 3. When the temperature was lowered to 83 K the linewidth was reduced by approximately a factor of 2 and the peak absorption increased, indicating that the integrated absorption was constant. These observations strongly indicate the single-phonon character of the absorption process as opposed to the strongly temperature-dependent multiphonon processes often observed in the far infrared.

As for other electro-optic crystals, \( 15 \) we expect that the large linear electro-optic coefficients \( 4 \) arise from the strong polar low-frequency vibrations of the ionic crystal and the polarizable electronic structure corresponding to the conjugated \( \pi \)-electron structure on the stilbazolium cation. This simple picture can be supported by investigation of the size and symmetry of the linear electro-optic tensor: An

In the DAST crystals, we expect that the simple vibration of the anion–cation pair corresponding to the reststrahlen band is the main cause of the strong absorption observed in the far infrared.
optical beam polarized along the stilbazolium cation (a axis) is efficiently modulated by a low-frequency field along the direction of the polar vibration (c axis), corresponding to a large nonlinear optical element $r_{113}$. The opposite geometry, corresponding to the element $r_{331}$, results in weak modulation. Unfortunately, efficient electro-optic modulation is limited at higher frequencies by the strong far-infrared absorption from the polar vibrations. Consequently, the practical phase-matched applications of DAST crystals will correspondingly be limited to the low-loss region below 0.5 THz. However, identifying the polar vibration of the organic salt as the cause of the strong far-infrared absorption also suggests new strategies for the synthesis of new electro-optic materials. Changing the weight of the anion–cation pair allows one to optimize the balance between resonant enhancement of the electro-optic modulation and loss owing to linear absorption of the modulating field.

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