

Electron–phonon coupling in the molecular charge transfer crystal 2-(α -methylbenzylamino)-5-nitropyridine

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ABSTRACT

Orientated single-crystal infrared, Raman and terahertz measurements have been carried out for the molecular charge transfer material 2-(α -methylbenzylamino)-5-nitropyridine. This information, together with experimental frequency doubling data and theoretical calculations of the electro-optic coefficient, was used to deduce the optical phonon contribution to the linear electro-optic coefficient. The optical phonon spectra are dominated by three intense bands attributed to vibrations of the ring, NO₂ substituent and N–H bond. The most intense scattering arose from the α_{bb} component of the polarisability tensor. This implied that the most significant contribution to the transition polarisability arises from the electronic transition near 435 nm, polarised along the *b*-axis of the crystal. The strongest bands in the infrared spectra are also associated with the same three bands. This implies that efficient electron-phonon coupling (or electronic delocalization) in the conjugated system. DFT calculations of optical phonon frequencies and eigenvectors were used to help assign relevant vibrational features and to derive useful information about the molecular structure. The information obtained from this study is important for assessing the suitability of this material for generating terahertz frequencies by optical rectification.

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1. Introduction

Molecular optically non-linear molecules have been the subject of intensive study for several decades. These charge transfer molecules, consisting of electron donor and acceptor groups separated by an extended, conjugated system of π electrons, have applications in the fields of photonics and optoelectronics [1], including frequency converters [2], Raman lasers [3] and electro-optic modulators [4].

The electro-optic effect in non-linear organic crystals is mainly electronic in origin, with smaller contributions from molecular vibrations and acoustic phonons. The subsequent fast response of these materials, combined with the intrinsically low dielectric constants, makes them attractive candidates for electro-optic devices in optical communications networks. This is in contrast to conventional ferroelectric inorganic materials such as lithium niobate, where the electro-optic response is dominated by acoustic phonon contributions. The low dielectric constant is particularly important in high-speed applications due to the resulting reduced device capacitance and lower velocity mismatch in optical waveguide switches and modulators.

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These materials often exhibit substantial linear electro-optic coefficients as well as second-order and third-order nonlinearities. The organic crystal 2-(α -methylbenzylamino)-5-nitropyridine (MBANP) is a typical molecular charge transfer material that has been studied for optical modulation [4], frequency doubling [5] and terahertz generation [6]. It also holds promise as a Raman laser converter with a large frequency shift of 3404 cm⁻¹ and a high damage threshold [2]. The first absorption in the near infrared is found near 1500 nm so the transparency range of MBANP extends from 450 nm to beyond 1500 nm. This molecule also exhibits wavelength dispersion of the optical indicatrix arising from different wavelength dispersion of the refractive indices in the three principal crystal directions.

Theoretical assessments of the non-linear optical behaviour of organic crystals, have established a relationship between the alignment of the molecular charge transfer axes and the magnitude of the various kinds of non-linear optical effect [7]. In the case of the linear electro-optic effect, optimum efficiency will be attained when the molecular axes are closely aligned and the low frequency electric field is applied in the direction of the resultant charge transfer axis. Departures from co-linearity of the molecular axes result in a progressive decrease in efficiency. In contrast, as the angle between the two axes increases, conditions for generating strong, phase-matched second harmonics are likely to be met,

the optimum efficiency corresponding to a half angle of 54.7° between the molecular axes.

In the case of the organic crystal MBANP, the maximum electric field induced polarisation will occur principally along the polar charge transfer axis of the pyridine system between the $-NH$ and the NO_2 groups. With this material, the half angle between the polar axes of two symmetrically non-equivalent MBANP molecules in the unit cell is quite large, at 33.5° . This results in moderate electro-optic coefficients which nonetheless, are comparable with those of inorganic crystals, and result in efficient THz generation [6].

Recently, molecular vibrations in organic non-linear optical materials have been shown to contribute significantly to the linear electro-optic coefficient [8]. For example, in the case of 4-(N,N-dimethylamino)-N-methyl-4'-toluene sulphonate (DAST) molecular vibrational modes have been estimated to contribute about 25% of the linear electro-optic coefficient r_{11} [8,9]. To contribute significantly, a vibrational mode must be intense and be both infrared- and Raman-active. Dielectric measurements on MBANP single crystals have shown that in addition to the electronic contribution which contributes the major part of the polarisability, there should be a substantial vibrational contribution [10]. In this paper, the linear and non-linear optical properties, and single crystal vibrational spectra of MBANP are studied with the aim of estimating the magnitude of the contribution of vibrational modes to the linear electro-optic effect in the infrared region.

There is a considerable body of information available on the MBANP family of organic materials, most of which can be grown into large, optically and chemically perfect crystals. MBANP has been well characterised structurally by X-ray [11–14] and neutron [14] diffraction, and optically [15,16]. Both the optical damage thresholds [16] and linear and second-order non-linear properties [17,18] have been evaluated. Oriented single-crystal Raman spectra and vibrational assignments have also been published [19]. The molecular structure of MBANP is shown in Fig. 1.

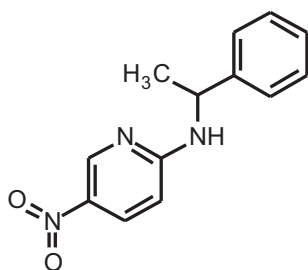
In general, the electro-optic coefficient, r , is made up of three contributions two of which are frequency dependent, thus:

$$r = r^e + r^o + r^a$$

r is the so-called free electro-optic coefficient that applies for frequencies lower than the lowest acoustic mode of the crystal. For frequencies above the acoustic mode (MHz range), where no acoustic modes are excited, the clamped electro-optic coefficient applies.

$$r^c = r^e + r^o$$

Above the highest optic mode frequency (100 THz), only electronic contributions to r are excited and we are in the field of non-linear optics. If, in common with most molecular crystals, we assume that the acoustic contribution, r^a , is small and can be neglected, r is equivalent to the clamped coefficient r^c .



Molecular structure of MBANP

Fig. 1. Molecular structure of MBANP.

2. Experimental details

MBANP was synthesised by reacting 2-chloro-5-nitropicoline with enantiopure α -methylbenzyl amine and purified by chromatography on silica [20]. It was grown into large single crystals as described previously [21].

The non-linear optical susceptibility d_{22} for MBANP single crystals was determined by the standard Maker fringe technique using $1.064 \mu\text{m}$ Nd:Yag laser radiation [5]. Using the quartz reference value of 0.30 pm V^{-1} at $1.064 \mu\text{m}$, the measured value of d_{22} for MBANP was $33.7 \pm 2 \text{ pm V}^{-1}$.

The room-temperature linear electro-optic coefficients for appropriately cut and polished MBANP single crystals, at low frequencies, were calculated from measured reduced half-wave voltages at 488, 514.5 and 632.8 nm [4]. The electric field was polarized along the monoclinic b -axis, a principal dielectric axis at all frequencies so the frequency dependent values measured were $\approx r_{22}$. Due to limitations posed by the size of the crystal used in the measurements, an effective value r_{eff} was obtained. The true value of r_{22} will be somewhat larger than r_{eff} . The experimental electro-optic coefficients are given in Table 1.

The absorption and refractive index along the b axis were measured for a 0.2 mm thick single crystal of MBANP between 0.5 and 3 THz, by optical rectification of 800 nm 40 fs pulses [6]. These are shown in Fig. 2. Electro-optic sampling was used for detection.

A refractive index of 2.25 ± 0.05 was measured at $80\text{--}100 \text{ cm}^{-1}$. Several phonon band absorptions were also observed between 40 and 100 cm^{-1} , which limits the efficiency of the crystal for THz generation. None the less, the measured efficiency was about 10 times that for the commonly used ZnTe crystal.

The infrared specular reflectance spectra in the range $800\text{--}6000 \text{ cm}^{-1}$ were measured on cut and polished (0 1 0) and (1 0 0) slabs with a BOMEM DA3 spectrometer [22]. The reflectance data were transformed to absorption by means of the Kramers–Kronig relation. The results for radiation polarised along the principal dielectric axes are shown in Fig. 3.

The infrared spectra of polycrystalline thin films of MBANP, from $550\text{--}3500 \text{ cm}^{-1}$, were also measured, with a resolution of $2\text{--}3 \text{ cm}^{-1}$, by means of a Perkin Elmer Paragon 1000 FTIR. The main

Table 1
Effective electro-optic coefficients for MBANP.

λ (nm)	n_y	$r_{\text{eff}} \approx r_{22}$ (pm/V)
488	1.9311	31.4 ± 0.1
514.5	1.8858	26.6 ± 0.1
632.8	1.7951	18.2 ± 0.2

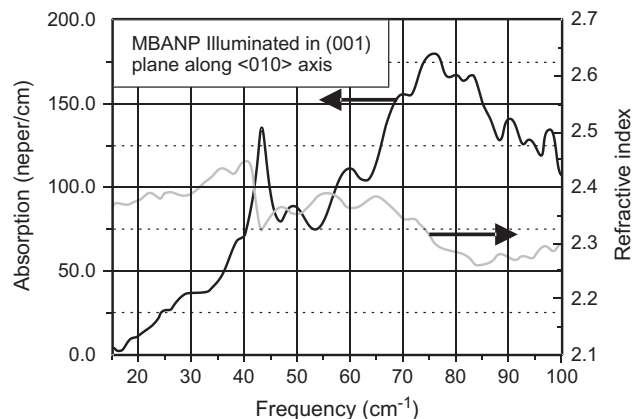


Fig. 2. Absorption and refractive index of single crystal MBANP between 0.5 and 3 THz.

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