

Article

# Broadband Anisotropic Optical Properties of the Terahertz Generator HMQ-TMS Organic Crystal

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**Abstract:** HMQ-TMS (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 2,4,6-trimethylbenzenesulfonate) is a recently discovered anisotropic organic crystal that can be exploited for the production of broadband high-intensity terahertz (THz) radiation through the optical rectification (OR) technique. HMQ-TMS plays a central role in THz technology due to its broad transparency range, large electro-optic coefficient and coherence length, and excellent crystal properties. However, its anisotropic optical properties have not been deeply researched yet. Here, from polarized reflectance and transmittance measurements along the  $x_1$  and  $x_3$  axes of a HMQ-TMS single-crystal, we extract both the refraction index  $n$  and the extinction coefficient  $k$  between 50 and 35,000  $\text{cm}^{-1}$ . We further measure the THz radiation generated by optical rectification at different infrared (IR) wavelengths and along the two  $x_1$  and  $x_3$  axes. These data highlight the remarkable anisotropic linear and nonlinear optical behavior of HMQ-TMS crystals, expanding the knowledge of its properties and applications from the THz to the UV region.

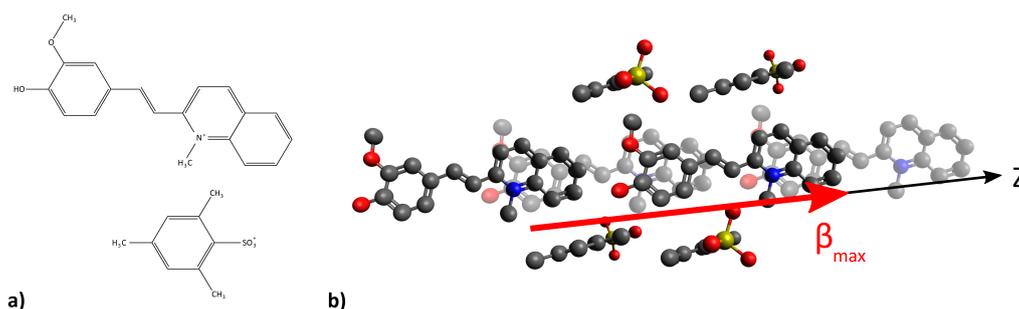
**Keywords:** terahertz; THz spectroscopy; optical indices; nonlinear effects; optical rectification; organic crystals; HMQ-TMS

## 1. Introduction

THz radiation (1 THz  $\sim$  33  $\text{cm}^{-1}$  or 4 meV photon energy) has gained over the years a considerable interest due to its broad variety of applications. Starting from fundamental scientific investigations, where THz can be used as a resonant probe for the plethora of excitations in condensed matter physics [1–3], its applications reach also to various industrial and biomedical activities [4–7], security applications [8–10], and particle-accelerator physics [11,12]. Following the growing interest, a rapid development of both THz generators and detectors has been made possible thanks to novel technologies that have become available in these last two decades, such as quantum cascade lasers, photoconductive antennas, Gunn lasers, and sources based on nonlinear optical (NLO) effects. The latter realm has been the starting point for the production of single cycle, high-intensity THz signals comparable to those obtained from free-electron facilities [13,14]. The process of difference frequency generation [15,16] or optical rectification (OR) [15,17–22] still holds the greatest interest due to its capabilities of reaching electric field magnitudes up to tens of MV/cm providing a broad THz spectral range going from nearly 0.1 THz up to 15 THz [1,23]. Due to these properties, novel

NLO materials have been highly investigated in terms of THz transparency and linear and nonlinear optical responses. As already highlighted in literature, the production of THz radiation through OR process is highly dependent on the material properties, like the microscopic optical response functions of the crystal [15,24]. The real and imaginary parts of the refractive index, both in the optical and THz emission regions, give information about the phase matching condition and the absorption effects inside the crystal. Therefore, the knowledge of those optical parameters is of great importance in order to optimize the OR process and the emitted THz spectrum. Moreover, many efforts are also required in order to optimize future growth processes of new THz crystals [25,26].

Among the many materials already discovered, like inorganic NLO crystals such as ZnTe and GaP [27], organic NLO crystals offer the best platform, mainly due to their strong nonlinear optical response arising from the molecules hyperpolarizability and orientation inside the crystal [15]. Organic crystals like DAST, DSTMS, OH1 [28–30], 2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 2,4,6-trimethylbenzenesulfonate (HMQ-TMS) [31] and BNA [32], are already widely used for THz photonics. Here, HMQ-TMS is an organic molecular crystal built upon HMQ (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium) cations and TMS (2,4,6-trimethylbenzenesulfonate) counter anions. HMQ-TMS shows a polar axis oriented along the  $x_3$  direction, as shown in Figure 1. Although the electromagnetic properties of HMQ-TMS have been partially studied [31,33,34], a complete investigation of its anisotropic optical properties is still missing. In recent works, Brunner et al. [33] estimated the crystal optical group index, with light polarized along the polar axis, through retardation of laser pulses [35], covering a range from 600 to 2000 nm. In addition, the absorption coefficient  $\alpha_3$  were also extracted from transmission measurements in the same spectral range and between 0.3 and 1.5 THz through THz time-domain spectroscopy. The same optical parameters have also been estimated for a broader THz spectral range (1.2–12 THz) in Reference [34]. In this paper, we extract from polarized reflectance and transmittance measurements, from THz to ultraviolet (UV), both the real (refraction index  $n$ ) and the imaginary part (extinction coefficient  $k$ ) of the complex refractive index  $\tilde{n} = n - ik$ , along the  $x_1$  and  $x_3$  (polar) axes of a HMQ-TMS single-crystal. We further measure the THz radiation generated by optical rectification at different infrared (IR) pumping wavelengths and along the two  $x_1$  and  $x_3$  axes. These data highlight the remarkable anisotropic linear and nonlinear optical behavior of HMQ-TMS crystal, as predicted from the crystallographic theory.



**Figure 1.** (a) Chemical structure of HMQ-TMS system. (b) Orientation inside the 2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 2,4,6-trimethylbenzenesulfonate (HMQ-TMS) crystal of the HMQ and TMS molecular groups projected on the crystallographic  $b$ -axis. A massive hyperpolarizability is associated to the HMQ chromophores, which are aligned along the polar axis  $x_3$  in such a way to define the maximum possible value of the order parameter  $\langle \cos^3 \theta \rangle$  [15].

## 2. Experimental Methods

### 2.1. Linear Response Study

The Reflectance ( $R$ ) and transmittance ( $T$ ) at room temperature of a HMQ-TMS single crystal have been measured, from THz to UV ( $50\text{--}35,000\text{ cm}^{-1}$ ), along the  $x_3$  and  $x_1$  axes. The crystal is characterised by a thickness of  $190\text{ }\mu\text{m}$  (as measured by a micrometer) and lateral dimensions of  $4\text{ mm} \times 2.5\text{ mm}$ . The face of incidence coincides with the crystallographic  $ac$ -plane, parallel to the radiation polarization. THz and Mid-Infrared (MIR) regions have been investigated at the SISSI Infrared beamline in Elettra Synchrotron (Trieste) through a Bruker Vertex 70V Michelson interferometer [36–38]. The region going from NIR to UV has been studied at the Physics Department of the University of Rome “La Sapienza” through a JASCO V-770 spectrometer. A calibrated gold (aluminium) mirror in the THz/MIR (NIR/UV) has been used as a reference in reflectance experiments. The linear complex refractive index as a function of frequency,  $n(\omega) - ik(\omega)$  (here  $\omega$  is a wavenumber), has been obtained from  $T(\omega)$  and  $R(\omega)$  data by deriving the exact analytical solution to the inverse problem for a slab under the approximation  $k^2 \ll n$  (no absorption at interfaces). The two indices can be expressed as [39]:

$$n(R, T, \omega) = \frac{1 + R_F(R, T)}{1 - R_F(R, T)} + \left\{ \frac{4R_F(R, T)}{[1 - R_F(R, T)]^2} - \left( \frac{1}{2\omega d} \right)^2 \ln^2 \left[ \frac{R_F(R, T)T}{R - R_F(R, T)} \right] \right\}^{1/2} \quad (1)$$

$$k(R, T, \omega) = \frac{1}{2\omega d} \ln \left[ \frac{R_F(R, T)T}{R - R_F(R, T)} \right], \quad (2)$$

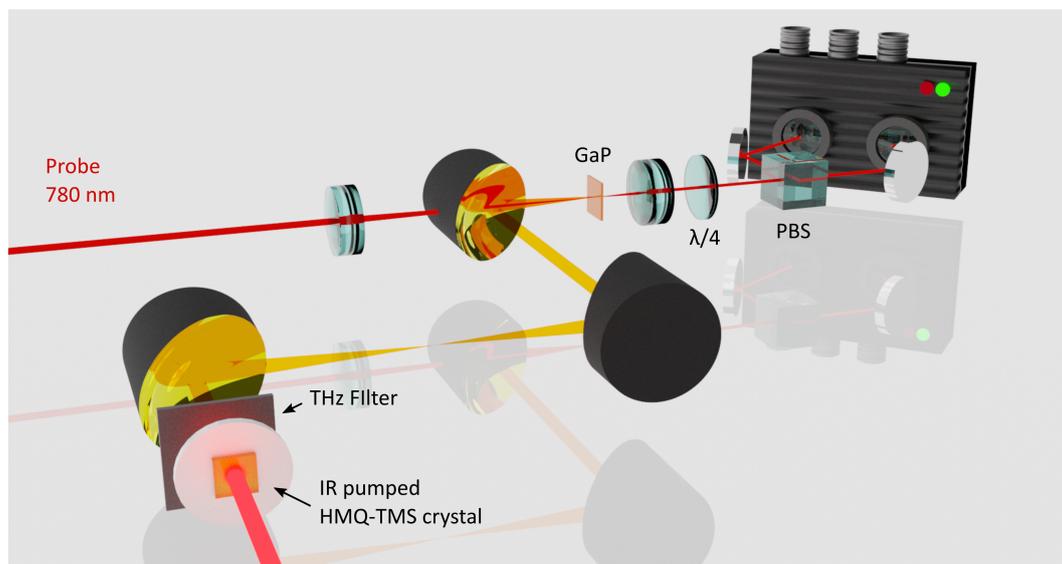
where  $d$  is the slab thickness and the single interface reflectance  $R_F$  takes the form

$$R_F = \frac{2 + T^2 - (1 - R)^2 - \{[2 + T^2 - (1 - R)^2]^2 - 4R(2 - R)\}^{1/2}}{2(2 - R)}$$

This method, based on both  $R$  and  $T$ , is independent from any major approximation. It is thus expected to be very precise in the determination of  $n$  and  $k$  values across the broad spectroscopic range.

### 2.2. Ir Pumping Scheme

In order to study the THz emission from the HMQ-TMS crystal, an optical apparatus has been developed based on a collinear optical parametric amplifier (OPA) from Light Conversion<sup>®</sup>, which permits the production of femtosecond pulses at tunable IR wavelengths, going from  $1200\text{ nm}$  up to  $1600\text{ nm}$ . The system is shown in Figure 2. A femtosecond high-intensity pulse at  $780\text{ nm}$  pumps the OPA, while a minor intensity is used for detection of the THz signal through the electro-optic effect in a GaP  $0.2\text{ mm}$  thick crystal. The signal emitted from the OPA is then used in order to pump the HMQ-TMS crystal at varying wavelengths. At constant fluence ( $4\text{ mJ}/\text{cm}^2$ ), the wavelength range spans from  $1300\text{ nm}$  to  $1600\text{ nm}$ , and four different values have been compared for the THz generation:  $1300, 1400, 1500$  and  $1600\text{ nm}$ , as suggested by previous literature [34].



**Figure 2.** Infrared (IR) pumping scheme for THz generation in a HMQ-TMS crystal. An initial 40 fs pulse at 780 nm, generated from a Ti:Sapphire laser (COHERENT® Legend Elite), is injected into the optical parametric amplifier (OPA) for the generation of IR femtosecond and high-fluence pulses. The residual pump is sent to the electro-optical detection system after passing through a delay stage and a series of optical elements. A GaP crystal is used for the detection.

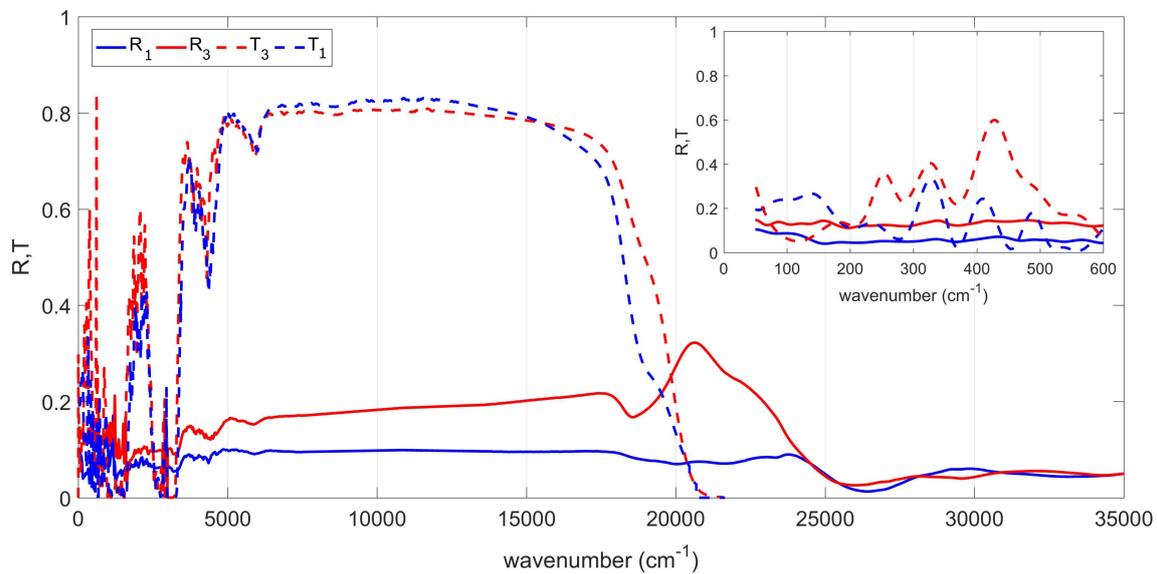
### 3. Results

#### 3.1. Linear Optical Parameters

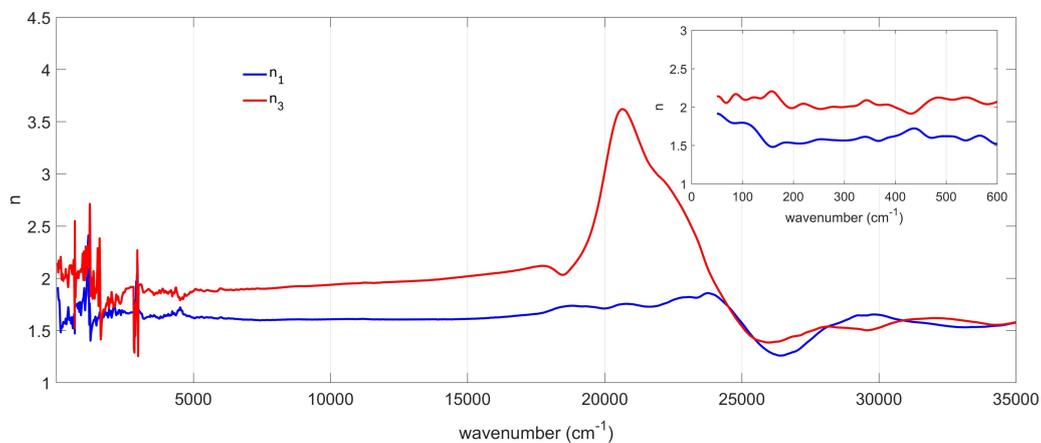
In Figure 3,  $R(\omega)$  and  $T(\omega)$  measurements for the HMQ-TMS crystal are reported between 50 and  $35,000\text{ cm}^{-1}$ . The blue (red) solid-lines concern R data, while blue (red) dashed-lines refer to T data with light polarization along the  $x_1$  and  $x_3$  axes, respectively. From the T measurements, one can notice a broad transparent spectral region extending from the mid-IR to the VIS region ( $5000\text{--}20,000\text{ cm}^{-1}$ ) for both axes, with a plateau at 83% along  $x_1$  and up to 80% along  $x_3$ , respectively. This slightly higher absorption is attributed to the major alignment of both HMQ cations and TMS anions along the  $x_3$  axis (see Figure 1) [31]. The first electronic transition is approximately located around  $20,000\text{ cm}^{-1}$  and corresponds to a strong reduction of transmittance along both axes, with a relatively low cut-off wavelength  $< 580\text{ nm}$ , in accordance with the estimation of Brunner et al. [33]. This electronic transition is related to the HMQ cations, which exhibit (in a methanol solution) an absorption maximum around  $439\text{ nm}$  (nearly  $22,000\text{ cm}^{-1}$ ) [31], mapping a smaller modulation of the reflectance (Figure 3) along the  $x_1$  axis. In the inset of Figure 3, a magnified plot of T (R) curves in the THz/MIR region is shown. Here, minima (maxima) correspond to both intra- and intermolecular (phonon) absorptions extending to the MIR region (see Figure 3).

In order to extract the real and imaginary parts of the refractive index from R and T data, the partial transparency of the HMQ-TMS single crystal in the MIR and VIS spectral region (see Figure 3) should be taken into account. Indeed, this transparency does not allow the use of Kramers-Kronig transformations. However, the complementary T and R data allow the derivation of an analytical method (see Equations (1) and (2) which considers Fresnel losses due to multiple reflections at the crystal surfaces [39]. The extracted optical parameters have been double-checked by using the RefFit constrained fitting program for a thin slab [40]. In Figure 4, the real ( $n$ ) part of refractive index along  $x_1$  (blue curves) and  $x_3$  (red curves) axes are shown. For both axes,  $n$  is nearly constant from MIR to red, showing an average value of 1.6 (2.0) for the  $x_1$  ( $x_3$ ) axis. A strong modulation of  $n$  can be observed between  $20,000$  and  $25,000\text{ cm}^{-1}$ , in correspondence to the electronic insulating gap. In the spectral range ( $5000\text{--}16,000\text{ cm}^{-1}$ ), and along the  $x_3$  axis, the refractive index behaves accordingly to already

published data [33]. Moreover, the inset of the same figure shows  $n$  in the THz/MIR spectral region, which behavior is in accordance with previous works [34].



**Figure 3.** Polarized T and R data of HMQ-TMS single crystal at room temperature along the  $x_1$  and  $x_3$  axis, in the 50–35,000  $\text{cm}^{-1}$  spectral region. T (R) data with light polarization along  $x_1$  and  $x_3$  are represented by dashed (solid) blue and red lines, respectively. In the inset, R and T data are plotted in the THz/MIR region.

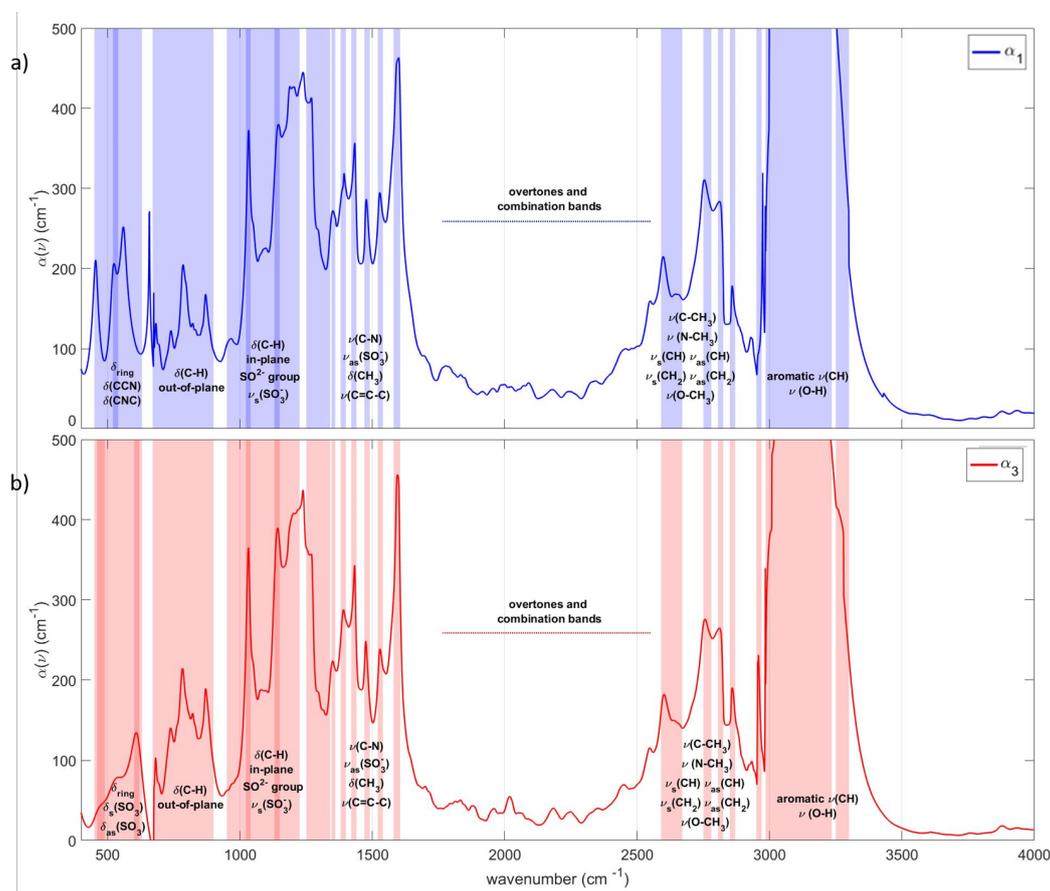


**Figure 4.** Real part of refractive index ( $n$ ) of the HMQ-TMS crystal at room temperature. Solid-blue (red) line corresponds to the value along the  $x_1$  ( $x_3$ ) axis. In the inset,  $n$  is plotted in the THz/MIR spectral range. The strong variation of  $n$  around 20,000  $\text{cm}^{-1}$  is generated by an electronic transition of the HMQ cations.

### 3.2. Spectral Analysis

The absorption coefficients, along both  $x_1$  and  $x_3$  axes, are calculated through the extinction coefficient  $k$  as  $\alpha = 4\pi\omega k$  ( $\omega$  is a wavenumber). They are reported in the spectral range 400–4000  $\text{cm}^{-1}$ , where most of the vibrational excitations of HMQ and TMS chemical groups fall (see Figure 5a,b). Differently to the electronic transitions that show a remarkable anisotropy (see Figure 4), the two vibrational spectra have several peaks in common. A small anisotropy can be observed only below 1000  $\text{cm}^{-1}$ , where ring-structure bending and lattice modes are located, and can be attributed to

molecules orientation. In order to assign those peaks, one can observe that aromatic rings in the HMQ-TMS structure (see Figure 1) show several C-H and C=C-C vibrational modes. Specifically, the bending modes of quinolinium ring are present below  $650\text{ cm}^{-1}$ . C-H out-of-plane and in-plane bending vibrations occur in the regions  $670\text{--}900\text{ cm}^{-1}$  and  $950\text{--}1225\text{ cm}^{-1}$ , respectively [41]. Along axis  $x_1$ , the band at  $528\text{ cm}^{-1}$  is identified with the C-N-C and C-C-N in-plane bending modes. For axis  $x_3$ , in the region  $450\text{--}600\text{ cm}^{-1}$ , two shoulders are distinguished at  $470$  and  $609\text{ cm}^{-1}$ , and assigned to the symmetric and asymmetric bending vibrations of the  $\text{-SO}_3$  group [42–44]. The peaks at about  $1030\text{ cm}^{-1}$ ,  $1140\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  can be assigned to the symmetric and asymmetric  $\text{SO}_3^-$  stretching, respectively [41]. Between  $1260\text{--}1340\text{ cm}^{-1}$ , three weak shoulders can be associated to aromatic primary amine C-N stretching. The peaks at  $1530$  and  $1590\text{ cm}^{-1}$  can be attributed to the vibrations of aromatic rings, while the absorptions around  $1390$ ,  $1430$  and  $1480\text{ cm}^{-1}$  are due to trimethyl  $\text{CH}_3$ . The shoulder at  $2652\text{ cm}^{-1}$  is related to the stretching vibration of C- $\text{CH}_3$ , located in the trimethylbenzenesulfonate. The methylamino N- $\text{CH}_3$  vibrational band is located at  $2760\text{ cm}^{-1}$ . Above  $2800\text{ cm}^{-1}$ , the C-H bonds vibrate with the methyl C-H symmetric and asymmetric stretching at  $2860$  and  $2960\text{ cm}^{-1}$ , respectively, and the methyl ether O- $\text{CH}_3$  and C-H stretching corresponding to the band at  $2815\text{ cm}^{-1}$ .



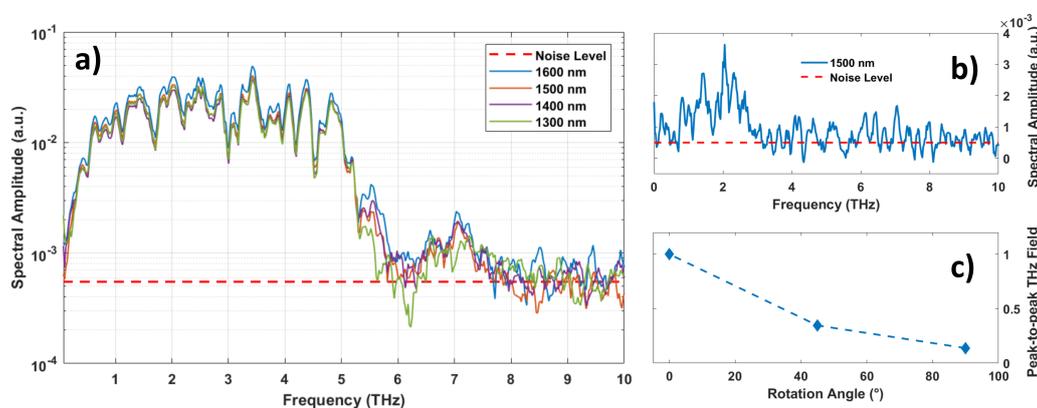
**Figure 5.** Absorption coefficients of HMQ-TMS crystal at room temperature in the vibrational spectral region  $400\text{--}4000\text{ cm}^{-1}$  along the polar  $x_3$  (a) and  $x_1$  (b) axes. The shaded area pictorially assigns the absorption peaks (or vibrational regions) to specific vibrational modes of HMQ and TMS chemical groups. (The labels are:  $\delta$  → bending vibration,  $\nu$  → stretching vibration,  $as$  → asymmetric,  $s$  → symmetric,  $ring$  → quinolinium ring).

The narrow peak at  $3000\text{ cm}^{-1}$  and the shoulder around  $3010\text{ cm}^{-1}$  are attributed to C-H bonds around the aromatic rings [41]. The region between  $3020\text{--}3230\text{ cm}^{-1}$ , related to aromatic C-H stretching and hydroxyl group vibrations, shows a very strong absorption that is nearly saturated. The small

shoulder, located at  $3250\text{ cm}^{-1}$ , can be attributed to O-H vibrational bonds. These general assignments are reported in Figure 5a,b.

### 3.3. THz Generation

For completeness, the nonlinear properties in terms of THz generation vs. different pumping wavelengths, along the  $x_1$  and  $x_3$  axes, have also been measured. Referring to the scheme of Figure 2, and varying the timing overlap between the THz pulse and the 780 nm probe in a GaP detection crystal, it is possible to scan the THz electric field magnitude in order to compute the spectral amplitude. The amplitudes along the  $x_3$  axis (coinciding with the maximum generation efficiency) at a fluence of  $4\text{ mJ/cm}^2$ , and at different IR pumping wavelengths (1300, 1400, 1500 and 1600 nm), are shown in Figure 6a. The comparable magnitudes of the field vs. the pumping wavelength suggest a nearly flat THz efficiency of the HMQ-TMs crystal in the whole infrared range.



**Figure 6.** (a) Spectral amplitude of the THz field generated by a HMQ-TMS single crystal pumped by a fs optical pulse at different IR wavelengths (1300, 1400, 1500 and 1600 nm). A broad frequency THz generation is visible from 0.5 up to 6 THz, with a further contribution around 7 THz. Minima in the spectra are mainly due to the water vapour absorption. (b) Spectral amplitude of the THz field generated along the  $x_1$  axis. The intensity and spectral bandwidth are strongly reduced in comparison to the  $x_3$  axis. Red-dashed lines in (a) and (b) represent the noise level in our experiment. (c) Peak-to-peak THz field magnitude vs the angle between the  $x_3$  axis and the pumping polarization. The THz field value strongly decreases for an increasing angle, indicating a strong reduction of the THz emission efficiency for a pump polarization along the  $x_1$  axis.

The anisotropic THz emission properties of HMQ-TMS have been studied by varying the crystal orientation with respect to the linearly polarized pump. In particular, both the incidence OPA polarization and the GaP detection crystal orientation have been kept fixed while the crystal has been rotated. Although we cannot exclude that some THz intensity might come from orientation misalignment and polarization losses, a small THz emission can be observed along  $x_1$  centered around 2 THz (Figure 6b) for a pumping wavelength at 1500 nm (similar data have been obtained at the other wavelengths). More specifically, the THz magnitude vs. the crystal orientation (Figure 6c) progressively decreases when the pumping polarization approaches  $x_1$ .

## 4. Conclusions

In this paper, we have measured the complex refractive index of a HMQ-TMS single crystal from terahertz to ultraviolet, both along the polar  $x_3$  axis and the orthogonal  $x_1$  axis on the crystallographic  $ac$ -plane. In the visible-ultraviolet region, we observe a remarkable anisotropy which is strongly attenuated in the infrared and terahertz range. The precise extraction of both the refractive indices and the absorption coefficients proposes an inverse problem approach for the THz generation study. Therefore, we have also measured the terahertz emission spectra along the same axes when pumping

in the infrared through a fs-amplifier laser. As expected from theoretical grounds, the THz emission shows a huge intensity reduction when the pumping polarization is parallel to the  $x_1$  axis. These data expand our knowledge of the HMQ-TMS optical properties across the broad spectral range from THz to UV, allowing a better understanding of its possible applications in THz pump-probe experiments of exotic electronic systems [45,46].

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**Conflicts of Interest:** The authors declare no conflicts of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

MDPI	Multidisciplinary Digital Publishing Institute
DOAJ	Directory of open access journals
TLA	Three letter acronym
LD	linear dichroism

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