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Nonlocal optical nonlinearity of ionic liquids

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Abstract

The nonlinear optical properties of two ionic liquids, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMI]BF₄) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMI]PF₆), have been investigated using the *Z*-scan technique. These compounds are liquid at room temperature and present a strong ionic nature. Nonlinear refraction and absorption, and thermo-optical measurements for both ionic liquids were performed using two different laser wavelengths, 514 nm and 810 nm, in the continuous wave and femtosecond regimes, respectively. It was observed that those specimens have large negative nonlinear refractive indexes and thermo-optical coefficients, but nonlinear absorption was not observed. Different dispersion relations were observed depending on the ionic liquid anion, which may be related to the distinct structures of these compounds. This result indicates that ionic liquids are suitable media for the investigation of nonlocal nonlinear phenomena.

1. Introduction

In recent years, the huge potential of organic materials (OM) in optical applications has motivated the development of new compounds and the study of their optical properties. The luminescent properties of OM have been exploited in laser media [1], markers for optical microscopy [2] and optical thermometry [3]. Owing to their large nonlinear optical properties, several applications have been proposed using OM, such as frequency conversion [4], optical limiting [5], optical modulators [6] and, recently, in the investigation of nonlocal effects [7, 8]. The origin of the OM nonlinearity can be attributed to light-induced molecular reorientation, incoherent electronic excitation and thermal lens effects [9]. Moreover, the knowledge of nonlinear optical properties does not only indicate whether the material is a good candidate for optical applications, but

it can reveal the internal structure of molecules and their interactions [10].

Among the myriad OM, a class of molten salts called ionic liquids has been intensively studied owing to their interesting physicochemical properties [11–22]. They present an ionic-covalent molecular structure and different molecular architectures [11]. They possess low melting point temperatures (below 100 °C), a relatively wide electrochemically stable window, good electrical conductivity, high ionic mobility, negligible vapor pressure, and excellent chemical and thermal stability. These materials are important for a large number of applications in chemistry and industry, such as in catalysis [12], batteries [13] and nanochemistry [14]. In the field of nanotechnology, they are very good stabilizers for colloids containing nanoparticles [15]. An important characteristic of these materials is that some of them possess liquid crystal properties [16, 17], which indicate that these compounds may present large nonlinear optical responses.

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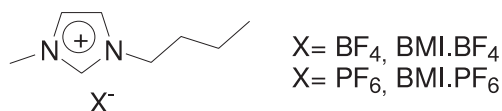


Figure 1. Schematic illustration of [BMI]BF₄ and [BMI]PF₆ ionic liquid structures.

However, their nonlinear optical properties are currently unexplored.

In this work, the nonlinear optical properties of two different ionic liquid compounds, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMI]BF₄) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMI]PF₆), have been investigated with the Z-scan technique [23]. The measurements were performed for two different excitation wavelengths, 514 and 810 nm, in the CW regime, and at 810 nm with femtosecond pulses. The origin of the observed large nonlinearity of these ionic liquids is discussed and their thermo-optical coefficients were also evaluated. Our results suggest ionic liquids as promising media for the investigation of optical nonlocal phenomena.

2. Experimental details

In figure 1 is depicted the structure of the studied IL. These halide-free ionic liquids were prepared following literature procedures and dried over molecular sieves (4 Å). The purity was checked with ¹H NMR spectra using the intensity of the ¹³C satellites of the imidazolium *N*-methyl group as an internal standard [18, 19]. The linear UV–vis absorption spectra of the studied compounds are depicted in figure 2. As can be seen in this figure, they are transparent in the UV–visible and near infrared regions. The laser wavelengths used in our experiments are also indicated in this figure.

The nonlinear optical properties of the ionic liquids were investigated using the Z-scan technique [23]. In this approach, the transmittance of a tightly focused Gaussian beam through a finite aperture in the far field is measured as a function of the sample position *z* with respect to the focal plane. At each position, the sample experiences a different light intensity. The phase imposed by the nonlinear refraction of the sample appears as a spatial beam broadening or narrowing in the far field. These beam shape changes modify the fraction of light that passes through a small aperture as the sample is moved along the beam propagation direction. From the transmittance curve are obtained the value and the signal of the medium nonlinear refractive index *n*₂. This quantity may have contributions of distinct origins, such as electronic or thermal effects. Removing the aperture in the far field it is possible to perform nonlinear absorption measurements.

The experiments were carried out using two different laser wavelengths, 514 and 810 nm. In the visible region, a CW argon laser was used, while in the near infrared region a CW, mode-locked, Ti:sapphire laser was employed as a light source, delivering pulses of 200 fs at a 76 MHz repetition rate. In this case, the pulse repetition rate could be reduced to the range of 100 Hz–10 kHz using a pulse selector. For both

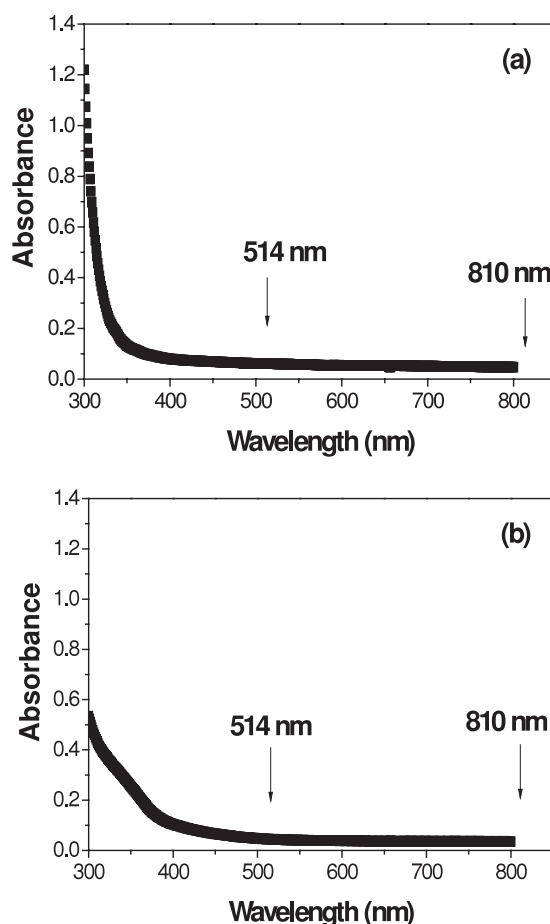


Figure 2. Linear absorption spectra of ionic liquids (a) [BMI]BF₄ and (b) [BMI]PF₆.

excitation wavelengths, the laser beam was modulated by a chopper and focused onto the sample by a convergent lens of 7.5 cm focal length. The sample consisted of the ionic liquid in a 1 mm quartz cell. It was mounted on a translation stage and moved around the lens focus (*z* = 0) by a computer controlled stepper motor. The light transmittance was then measured using a closed aperture photodetector as a function of the sample position. The detected signal was amplified by a lock-in amplifier and then processed by a computer. Nonlinear absorption measurements were performed using the same experimental setup but without the aperture.

3. Results and discussion

The obtained normalized transmittance curves, as a function of the sample position, are presented in figure 3 for 514 nm and figure 4 for 810 nm for [BMI]BF₄ (a) and [BMI]PF₆ (b) samples. In both cases, the sample position is normalized with respect to the Rayleigh length, and from the observed transmittance variations [23], the nonlinear refractive index values *n*₂ were evaluated. For CW laser excitation tuned at 514 nm, the [BMI]BF₄ presented an *n*₂ equal to $-2.8 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1}$, while for [BMI]PF₆ this value was $-9.7 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1}$.

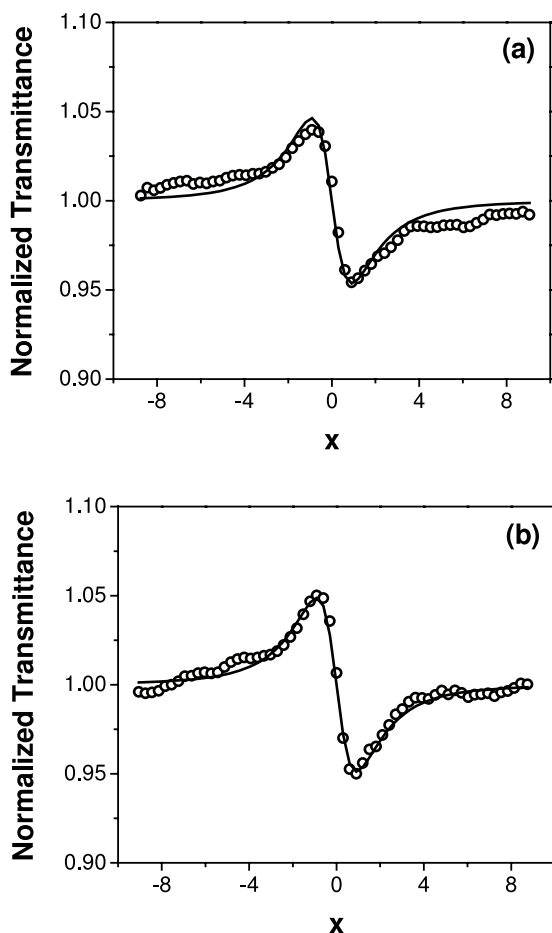


Figure 3. Z-scan curve for the ionic liquids (a) [BMI]BF₄, $P_{\text{laser}} = 26.2$ mW and (b) [BMI]PF₆, $P_{\text{laser}} = 8.91$ mW at 514 nm. Open circles correspond to experimental data while solid lines show the theoretical fit.

The Z-scan results revealed different n_2 values for high repetition rate (76 MHz) femtosecond laser excitation at 810 nm. From the curves in figure 4, the measured values for the nonlinear refractive index of [BMI]BF₄ and [BMI]PF₆ were equal to $n_2 = -1.8 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1}$ and $n_2 = -2.7 \times 10^{-9} \text{ cm}^2 \text{ W}^{-1}$ respectively. The dispersion in n_2 value was expected owing to the fact that neither laser wavelength is resonant with any energy level of these compounds.

Nevertheless, when the laser repetition rate was reduced into the range of 100 Hz–10 kHz in our experiments, surprisingly, no Z-scan curve was obtained. The results suggest that ultrafast effects contribute very little to the nonlinear refractive index of these ionic liquids. Indeed, the modulus of the ultrafast nonlinear refractive indexes of such compounds must be smaller than $5 \times 10^{-17} \text{ cm}^2 \text{ W}^{-1}$, which was our Z-scan system resolution. Moreover, a cumulative effect concerning the laser pulses gives the most important contribution to the observed nonlinearity.

Z-scan measurements with the open aperture configuration were also performed. However, nonlinear absorption was not observed at any of the experimental conditions exploited in this work.

The origin of this large and slow nonlinearity is discussed as follows. It is expected that molecules with delocalization of

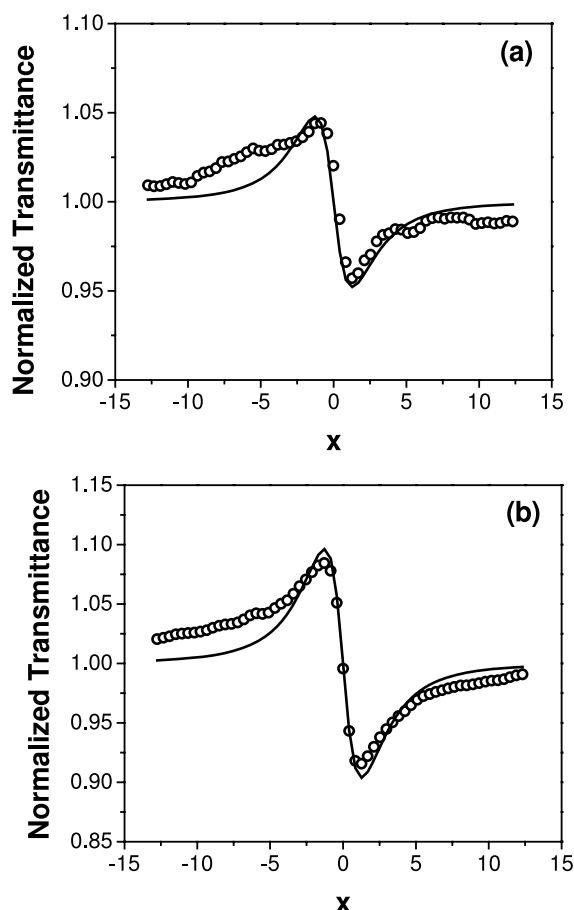


Figure 4. Z-scan curve for the ionic liquids (a) [BMI]BF₄, $P_{\text{laser}} = 74.6$ mW and (b) [BMI]PF₆, $P_{\text{laser}} = 94.8$ mW at 810 nm. Open circles correspond to experimental data while solid lines show the theoretical fit.

positive and negative charges possess large electronic nonlinear optical responses [23]. This nonlinearity is related to an optically induced transition of the molecule, in such way that a large variation of the molecule dipole occurs upon laser excitation, leading to refractive and absorptive nonlinear optical responses. However, the electronic and the light-induced molecule reorientation contributions to the optical nonlinearity present an ultrafast relaxation in liquids and it does not depend on the laser repetition rate typically [23–25]. Owing to our experimental results, we can conclude that this electronic excitation does not occur in the studied ionic liquids and the origin of their large nonlinearity cannot be attributed to electronic effects.

On the other hand, the thermal lens effect originates usually slow optical responses (tens of μs), and these are related to the temperature variation along the studied medium, which grows as the laser repetition rate increases [23, 26–29]. This effect gives often a negative nonlinearity contribution, as the increase of temperature induces a decrease of refractive index of the medium. While in Z-scan experiments the observed peak–valley distance is approximately equal to $1.7z_0$ owing to an electronic origin of the nonlinear response, larger values are obtained in the case of thermal nonlinearities. Indeed, although no Z-scan curve was obtained in the

Table 1. Ionic liquids optical and thermal properties.

Medium	κ (W m ⁻¹ K ⁻¹)	λ (nm)	α_0 (cm ⁻¹)	n_2 (cm ² W ⁻¹)	(dn/dT) (K ⁻¹)
[BMI]BF ₄ 0.1785 [30]		514	0.029	-2.8×10^{-9}	-1.04×10^{-3}
		810	0.014	-1.8×10^{-9}	-2.0×10^{-4}
[BMI]PF ₆ 0.109 [31]		514	0.054	-9.7×10^{-9}	-1.05×10^{-3}
		810	0.032	-2.7×10^{-9}	-8.1×10^{-5}

femtosecond regime at low repetition rate, a large negative nonlinear refractive signal was observed when the laser repetition rate was very high (76 MHz) or in the CW regime. In these cases, the observed peak–valley distance was about $1.81z_0$ and $2.55z_0$ for both ionic liquids at 514 and 810 nm, respectively. The results indicate that the thermal lens effect gives the most important contribution for the large nonlinearity that this medium presents.

The thermo-optical coefficient (dn/dT) for the studied compounds was also evaluated. For CW and ultrahigh repetition excitation, the thermal contribution for the transmittance in Z-scan experiments can be given by [27–29]

$$T(x) = \left\{ 1 + \frac{\theta}{2} \tan^{-1} \left[\frac{2x}{(9+x^2)(1+x^2)/2\tau + (3+x^2)} \right] \right\}^2, \quad (1)$$

where θ is the thermally induced phase shift, $x = z/z_0$ and $\tau = t/t_{c0}$ are the normalized distance and time respectively, $t_{c0} = \frac{w_0^2}{4D}$ corresponds to the characteristic thermal lens time constant, w_0 is the beam waist and D is the thermal diffusivity of the medium. From the curve of the normalized peak–valley distance (Δx_{p-v}) as a function of the normalized time for linear absorption processes [29] and the Δx_{p-v} obtained from figures 3 and 4, the values of τ were evaluated. Using equation (1) to fit the results of figures 3 and 4, the value of θ can be obtained for both laser excitations. In the absence of fluorescence, the thermo-optical coefficient is then calculated using

$$\frac{dn}{dT} = -\frac{\lambda \kappa}{P \alpha_0 L_{\text{eff}}} \theta, \quad (2)$$

where κ and α_0 are the heat conductivity and linear absorption coefficient respectively, P is the laser power, and $L_{\text{eff}} = (1 - e^{-\alpha_0 L})/\alpha_0$ is the sample effective length. Table 1 summarizes the thermal conductivities [30, 31] and the measured optical properties for both samples. In particular, the thermo-optical coefficient values concerning [BMI]BF₄ are corroborated by a previous work [30].

A comparison between the obtained values shown in table 1 reveals that, although these compounds are similar, their nonlinear and thermo-optical dispersion relations are very different in this range of wavelengths. This could be related to their peculiar structural supramolecular organization in which a more diverse set of floating nanostructure aggregates [32] is expected for the octahedral PF₆ anions that possess at least two different hydrogen bond sites as compared to the four equivalent F sites of the tetrahedral BF₄ anion [33, 34]. This structural organization yields liquids with quite different physicochemical properties such

as melting points, hydrophobicity and stability. For example, the hexafluorophosphate salt is hydrophobic whereas the tetrafluoroborate analog is hydrophilic [35, 36].

Although thermal nonlinearity is not suitable for ultrafast photonic applications, its nonlocal character has been intensively investigated in recent years [7, 8, 37–42]. Indeed, materials that have thermo-optical responses may present a large spatial nonlocality on the refractive index change as a consequence of heat conduction process. There are several interesting effects that can be attributed to nonlocal nonlinearities, for example, stabilization and interaction of complex solitons [7, 37, 38], prevention of multidimensional beam collapse [39] and shock waves [40–42]. In the present work, we observed that both ionic liquids present large nonlinearities, with a nonlocal character. This result, added to their low values of linear and nonlinear absorption, indicates that ionic liquids are promising candidates for the development of optical nonlocal applications.

4. Conclusion

In summary, we have carried out the first investigation of the nonlinear optical properties of two different ionic liquids using the Z-scan technique for two excitation wavelengths, 514 and 810 nm. Large nonlinear refractive indexes, of thermal origin, were obtained for both wavelengths. Nonlinear absorption has not been observed in all experimental configurations. The thermo-optical coefficients of both compounds were also evaluated. The results revealed that different ionic liquid structures, determined by the anion, influence the nonlinear refractive index and thermo-optical coefficient dispersion. Moreover, the values obtained suggest that ionic liquids are a class of very promising materials when aiming at nonlocal optical applications.

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