CW Z-scan measurements in ionic liquids

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Abstract

We report on the first investigation of the nonlinear optical properties of ionic liquids, using the Z-scan technique. These compounds are liquids at room temperature and present a strong ionic nature. Nonlinear refraction and absorption measurements of two kinds of ionic liquids were performed for two different laser wavelengths, 514 and 810 nm, in the CW regime. The results showed that those specimens have large negative nonlinear refractive indexes, in the order of 10^{-8} to 10^{-9} cm^2/W for both laser wavelengths, however nonlinear absorption was not observed.

Introduction

A large number of photonic applications have been developed based on the nonlinear optical properties of materials. Different kinds of media have been studied and engineered aiming their use in photonics devices. Among the myriad of studied compounds, organic materials (OM) are of great importance due to their large optical nonlinearities and fast responses [1]. However, a large number of OM has their optical properties currently uninvestigated, as ionic liquids for instance.

Ionic liquids are liquid compounds that display ionic-covalent crystalline structures [2]. They have 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 catalysis, batteries, chemical analysis and as a stabilizer for colloids containing nanoparticles.

An important characteristic of these materials is that some of them possess liquid crystal properties [3,4], which indicate that these compounds may present large nonlinear optical responses. In this work, we investigated the nonlinear optical properties of two different ionic liquid compounds using the Z-scan technique [5]. The measurements were performed for two different excitation wavelengths, 514 nm and 810 nm, in the CW regime. The origin of the observed large nonlinearity of these ionic liquids is also discussed.

Experimental Setup

In the Z-scan technique 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 nonlinear refraction of the sample causes a spatial beam broadening or narrowing in the far field and thus modifies the fraction of light that passes through the aperture as the sample position is changed. A typical peak-valley (valley-peak) transmittance curve is obtained when the nonlinear refractive index of the medium is negative (positive). In the limit where the sample can be considered thin, compared to the beam Rayleigh length ($L < z_0$), it is possible from the peak to valley variation of the measured transmittance curve to evaluate the maximum nonlinear phase-shift and hence, knowing the incident laser power, to obtain the nonlinear refractive index n_2 [5,6]. Removing the aperture in the far field it is possible to perform nonlinear absorption measurements. Such Z-scan traces are expected to be symmetric with respect to the focal point (z = 0) where they exhibit a minimum transmittance in the case of nonlinear absorption (multiphoton absorption) and a maximum for the saturation absorption. For media exhibiting both nonlinear refraction and absorption properties, a closed aperture Z-scan measurement is sensitive to both effects. Dividing the closed aperture data by the open aperture one yields a Z-scan trace typical of a purely refractive nonlinearity [5].

The experimental setup used to measure the nonlinear refractive index and absorption of our ionic liquid samples in this work is depicted in the Figure 1. A CW Argon laser (Ti:sapphire laser) operating at 514 nm (810 nm) was used as a light source. 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 a 1 mm quartz cuvette within a small amount of our materials under investigation. 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 by 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 using an opened aperture configuration.

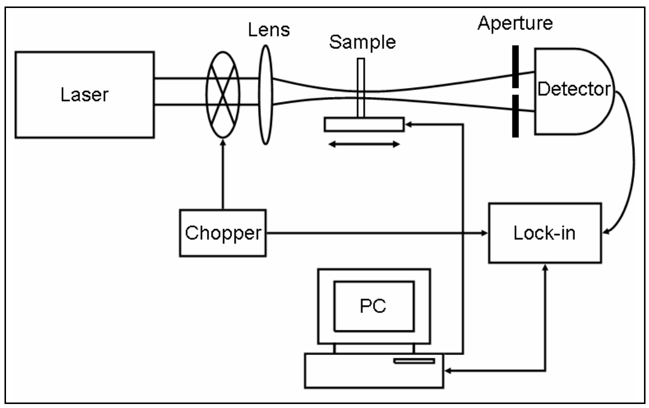

Figure 1: Experimental setup for optical nonlinearity measurements using Z-scan technique.

Results and Discussions

Two kinds of ionic liquids were investigated in this work: 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF_4) and 1-n-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6). The chemical structure of these compounds is presented in Figure 2, where X corresponds to BF_4 or PF_6.

Figure 2: Chemical structure of the ionic liquid.

The linear UV-VIS absorption spectra of the ionic liquids BMI-BF_4 and BMI-PF_6 are presented in Figure 3. 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.

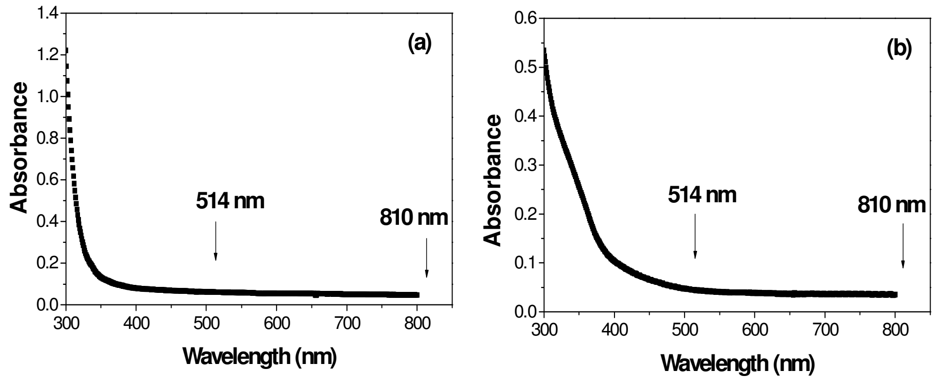

Figure 3: Linear absorption spectra of ionic liquids (a) BMI-BF_4 and (b) BMI-PF_6.

Figure 4 shows the typical normalized transmittances, closed aperture, as a function of the sample position, for CW laser excitation tuned at 514 nm, for BMI-BF_4 and BMI-PF_6 ionic liquids. From the observed transmittance variations, the nonlinear refractive index values n_2 were evaluated to be -3.7 x 10^{-9} cm^2/W and -2.0 x 10^{-8} cm^2/W, respectively. Although this value is smaller than other materials, such as photorefractive crystals and chinese tea, this nonlinearity is much larger than several organic liquids as DMSO and CS_2, for example.

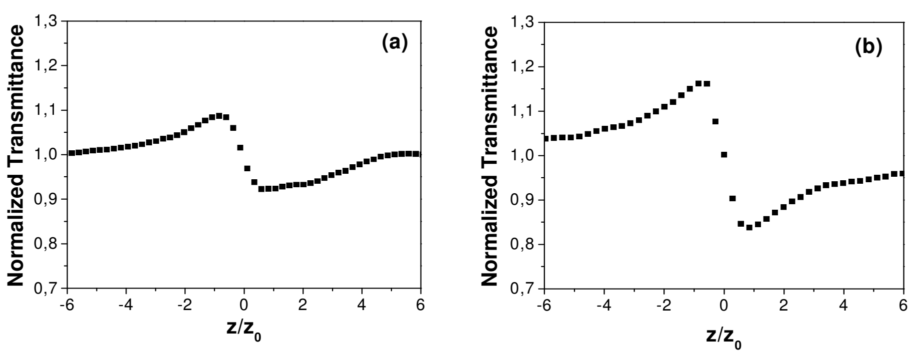

Figure 4: Z-scan curve for the ionic liquids (a) BMI-BF_4, P_{laser} = 25.4 mW and (b) BMI-PF_6, P_{laser} = 15.2 mW at 514 nm.

Typical Z-scan curves obtained for CW laser excitation tuned at 810 nm for both BMI-BF_4 and BMI-PF_6 are presented in Figure 5. The BMI-BF_4 ionic liquid presented a nonlinear refractive index value n_2 = -3.0 x 10^{-9} cm^2/W which is of the same order of magnitude that at 514 nm. However, for the BMI-PF_6, the measured nonlinear refractive index at 810 nm was n_2 = - 4.0 x 10^{-9} cm^2/W, which is much smaller than what was observed in the former case.

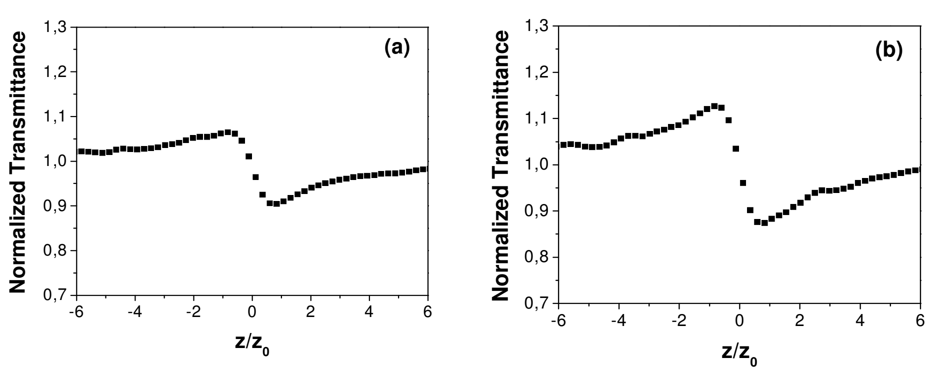

Figure 5: Z-scan curve for the ionic liquids (a) BMI-BF_4, P_{laser} = 73.7 mW and (b) BMI-PF_6, P_{laser} = 87.3 mW at 810 nm.

We also performed the Z-scan measurements with the opened aperture configuration. In this case, nonlinear absorption was not observed at any experimental conditions exploited in this work.

As the carried measurements were performed only in CW regime, the origin of this large nonlinearity is not completely understood up to now. We believe that thermal effects give the main important contribution to the measured value of n_2; however, only after experiments in pulsed regime we would be able to quantify the electronic and thermal contributions more accurately. Another interesting point is that, for the sample BMI-PF_6, the value of n_2 is larger when the laser is tuned at 514 nm than at 810 nm, while the value is almost the same, within the experimental error, for the sample BMI-BF_4. This result suggests that although the compounds are similar, their nonlinear dispersion relations are very different in this range of wavelengths.

Conclusions

We have carried out the first investigation, to the best of our knowledge, of the nonlinearity optical properties of two different ionic liquids using the Z-scan technique for two excitation wavelengths, 514nm and 810 nm, in the CW regime. Large nonlinear refractive indexes were obtained for both wavelengths. This result suggests that this nonlinearity is mainly due to thermal effects, although experiments in pulsed laser regime are needed in order to confirm this assumption. No nonlinear absorption was observed for all experimental configurations.

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