Nonlinear absorption in bis(1-butyl-3-methylimidazolium) tetrathiocyanatozincate ($[BMIM]_2[Zn(SCN)_4]$) an ionic liquid with a transition metal in the anionic moiety

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Abstract

Nonlinear absorption has been detected and characterized by open aperture Z-scan in ionic liquids obtained by combination of 1-butyl-3-methyl-imidazolium cations with anions containing a transition metal (Zn) and thiocyanato groups. The laser source was a Ti:Sapphire oscillator (80-fs pulses, λ=810nm, repetition rate of 80.75MHz). This ionic liquid presents quite low heat capacity that favours the development of strong thermal effects at 810nm. Thermal effects and nonlinear absorption make the ionic liquid interesting for optical limiting purposes.

1. Introduction

The synchronized absorption of two or more photons by an active molecule reaching temporarily an excited state via intermediate states is known as multiphoton absorption (MPA), an intensity-dependent and non-parametric nonlinear effect [1]. Although it is a limiting factor in nonlinear optical devices, it is very useful in applications like frequency up-conversion lasing, data storage, microfabrication, fluorescence microscopy, optical limiting, optical reshaping or optical stabilization (see for example [1,2] and references therein). In the last twenty years, a lot of effort has been directed to the research on multiphoton absorbing materials such as organic liquids, liquid crystals, polymers, fullerenes, organometallic compounds and biomolecules [1,3].

During the last ten years, a particular kind of salts known as ionic liquids (IL) have been the object of interest of numerous research groups [4,5]. Typically, ILs are composed by a large cation (usually organic, containing nitrogen, sulphur or phosphorous and one or more alkyl chains) and an anion which can be mono or polyatomic, organic or inorganic. These emergent materials are involved in interesting applications in fields as electrochemistry, nuclear processing or renewable energies. The technologic development around them has required an enormous effort in the synthesis and in the characterization of their chemical and physical properties, needed for designing any application. Among them, optical properties have been addressed only by few researchers. Optical absorption and fluorescence have been studied in a limited set of imidazolium-based ionic liquids [6,7], and thermooptic effect induced by different laser sources have been addressed in [8-14]. Nonlinear absorption has not been detected in any of the liquids characterized in those papers at the selected wavelengths. Nevertheless, Sesto and co-workers have designed phosphonium based ionic liquids with cubic susceptibilities basing on the cubic susceptibilities of the constituent ions [15,16]. They report the existence of nonlinear absorption in some of them but they did not provide, up to our knowledge, quantitative values of neither the nonlinear absorption coefficient nor the nonlinear cross section. In this work, we study the nonlinear absorption effects in an ionic liquid containing a Zn atom in the anionic moiety and 1-butyl-3-methyl-imidazolium [BMIM] as cation.

2. Results and discussion

As there were no reported preparations for the IL of our interest, we proceed to the synthesis of $BMIM_2Zn(SCN)_4$ (Figure 1) which was carried out by treating BMIMCl and KSCN in acetone with anhydrous $ZnCl_2$ under reflux.

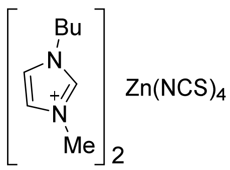

Figure 1

Heat Capacity: The sample was subjected to temperature ramps at 0.25 $K \cdot min^{-1}$ in the temperature interval (280-338) K using a DSCIII calorimeter from Setaram. From these experiments, heat capacity can be determined. Moreover, information about any physical or chemical process which involves heat exchange –in particular, phase transitions– can be obtained. We estimated the uncertainty of heat capacity measurements in about 0.05 $J \cdot g^{-1} \cdot K^{-1}$, much higher than that usually found for other using this procedure, [17,18] fact which comes from the difficult handling of ILs.

We found that the compound present quite low values, (see Table 1), which makes them quite sensitive to heating and, particularly, to that induced by laser pulsed radiation, as it is shown below.

Table 1

T/K	c_p/ $J\cdot g^{-1}\cdot K^{-1}$
283.15	1.53
298.15	1.57
313.15	1.61
333.15	1.64

Linear absorption: The absorption coefficient was retrieved starting from the transmittance data measured with a Perkin Elmer lambda25 spectrometer. The absorbance range is up to 3.2. The used interval of wavelengths is 300-1000nm (the device allows operating from 190-1100nm).

The absorbance spectrum from 280nm-1000nm is shown in Figure 2. The pathlength of the cells was 1mm. The liquid present negligible linear absorbance at the excitation length, 810nm.

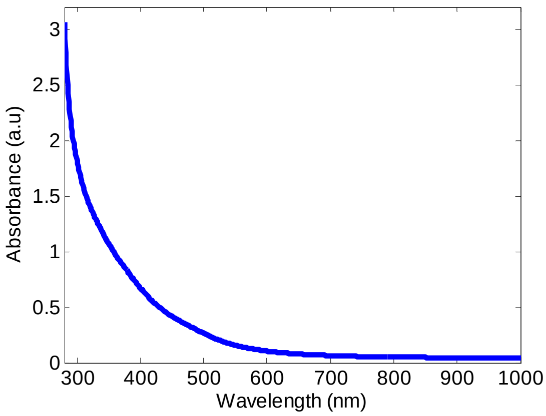

Figure 2

Refractive index: it was measured by a multi wavelength Abbe refractometer, model ATAGO DR-M2, resulting in the value n_0~1.55 at 680nm.

Nonlinear absorption: The characterization of nonlinear absorption has been conducted with open aperture Z-scan technique[19]. A Ti:sapphire oscillator delivers pulses of $\tau_0 = 80$ fs (FWHM) with a central wavelength of $\lambda_0 =$ 810 nm and with a repetition rate of 80.75 MHz. The laser beam was focused by a positive lens to a Gaussian spot of 17 μm of radius (at $1/e^2$ in intensity). The sample, a 1 mm quartz cell filled with the IL, is moved with a motorized translation platform from a position behind the focus towards a position ahead it, with 1 mm step. A photodiode detector measures the power transmitted by the sample as function of the relative position between the sample and the focus.

In Figure 3 we plot the open aperture Z-scan curve obtained with this ionic liquid together with the fit to theoretical model for three-photon absorption. The values of the absorption coefficients estimated by this fit is β_{3PA}= (1.4±0.5) 10^{-3} cm^3/GW^2.

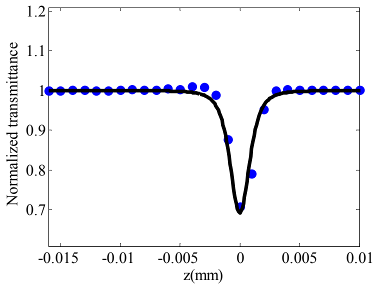

Figure 3

3. Conclusions

Nonlinear absorption has been detected in this newly synthesized ionic liquid. The absorption coefficient has been characterized by the open aperture z-scan technique at 810 nm. The behaviour observed is compatible with three photon absorption. The order of magnitude of the value of the nonlinear absorption coefficient is similar to the measured in other Zn compounds at the same wavelength, ZnO or ZnS, or TiO_2.

Experimental

Synthesis of bis(1-butyl-3-methylimidazolium) tetrathiocyanatozincate [BMIM]$_2$[Zn(SCN)$_4$]

A mixture of BMIMCl (5.220 g, 30 mmol), KSCN (7.995 g, 82 mmol) and anhydrous $ZnCl_2$ (2.025 g) in acetone (250 mL), was refluxed for 5 h. The reaction mixture was filtered off, the solvent evaporated and the residue dissolved in dichloromethane and filtered off. The evaporation of the solvent under vacuum afforded $[BMIM]_2[Zn(SCN)_4]$ as a clear oil (7.900g, 93%). ^{1}H NMR (300MHz, DMSO-d_6) δ: 9.03 (s, 1H Im-H2), 7.68 (t, 1H, J= 1.7 Hz), 7.62 (t, 1H, J= 1.7 Hz), 4.16(t, 2H, J= 7.2 Hz), 3.85 (s, 3H, NMe), 1.85-1.73 (m, 2H), 1.30 (hex., 2H, J= 7.5 Hz), 0.90 (t, 3H, J= 7.3 Hz). ^{13}C NMR (75 MHz, DMSO-d_6) δ 137.20, 135.33, 124.31, 122.99, 49.48, 36.49, 31.99, 19.46, 13.77. IR (goldengate) cm^{-1}: 3143, 2958, 2933, 2831, 2063, 1566, 1461, 1162, 744, 648. MS (electrospray, positive) m/z (%): 717 (20), 715(26), 713 (24, $BMIM_3Zn(SCN)_4$), 336(10, $BMIM_2SCN$), 293(50), 291(21), 186 (100). MS (electrospray, negative ion) m/z (%): 439(4), 437(5), 435(8, $BMIMZn(SCN)_4$), 242(47), 240(70), 238(100) $Zn(SCN)_3$.

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