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Low-temperature photoluminescence of *p*-nitroaniline and *o*-methyl-*p*-nitroaniline crystals

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Abstract

Photoemission spectra of *para*-nitroaniline (*p*-NA) and *ortho*-methyl-*para*-nitroaniline (MNA) single crystals measured between 5 and 250 K revealed that the MNA crystals emit phosphorescence and fluorescence in contrast with the *p*-NA crystals which have only fluorescence. It is assumed that the fluorescence of *p*-NA crystals at 5 K originates from the doublet state of negatively charged polarons while the fluorescence of MNA crystals at 60 K is due to trap states. The Stokes shift between absorption and emission onsets, measured at 5 K, is much larger in the *p*-NA crystals than in the MNA and *meta*-nitroaniline (*m*-NA) crystals. This fact is rationalized by different geometrical changes caused by excitation.

Keywords: *p*-Nitroaniline; *o*-Methyl-*p*-nitroaniline (MNA); *m*-Nitroaniline; Molecular crystals; Low-temperature photoemission; Semiempirical calculations of electronic transitions and molecular dipole moments; Stokes shifts; Geometry of excited states; Planarity; Polarons; Trap states

1. Introduction

Nitroanilines belong to the so-called push–pull molecules due to the intramolecular charge transfer (ICT) from the $-NH_2$ electron-donor group, through the phenyl ring, to the electron-acceptor $-NO_2$ group. *para*-Nitroaniline (*p*-NA) and *meta*-nitroaniline (*m*-NA) serve as the reference compounds in both, experimental and computational, studies on optical nonlinearity [1–3]. Photoluminescence properties of nitroanilines are however still the subject of intensive studies. In the seventies of the XX century, McGlynn et al. [4] observed fluorescence of *o*-NA and *m*-NA in polar glassy media at 77 K, but the only emission of *p*-NA observed under the same experimental conditions was phosphorescence. Electronic absorption and emission spectra of nitroanilines depend on the polarity of the medium. This phenomenon is related to the proximity of the lowest energy excited singlet (and triplet) states of different character, $n–\pi^*$ and $\pi–\pi^*$ [5,6]. In the case of *p*-NA in weakly polar solvents the lowest energy singlet has $n–\pi^*$ character and fluorescence was not observed because of the fast intersystem crossing [7,8]. The solvent effect on the electronic excited states explains the character of electronic absorption and emission as well as the first order hyperpolarizability of *p*-NA [9–11]. In contrast with nitroanilines in solutions, the electronic spectra of their crystals were studied only scarcely. The polarized electronic absorption spectra of the *m*-NA [12] and *p*-NA [13] single crystals were examined by Bertinelli et al. The directional dispersion of charge transfer (CT) excitons was detected in the *p*-NA crystals [14].

The substitution of a methyl group to *p*-NA in the *ortho* position relative to the amino group delivered a material with enhanced optical nonlinearity compared to the parent molecule. This compound, *ortho*-methyl-*para*-nitroaniline (MNA), crystallizes in the non-centrosymmetric structure and reveals the efficient second harmonic generation (SHG) [15] and the strong linear electrooptic (Pockels) effect [16]. Some information on its electronic states can be extracted from the visible transmission [16], polarized reflectance and electroreflectance spectra [17] of single crystals. The intra- and intermolecular electronic transitions were calculated for the MNA molecular clusters [18].

Our previous emission studies of the *m*-NA and *meta*-nitrophenol single crystals at 5 K revealed the phosphorescence and fluorescence bands positioned in disagreement with the Stokes law [19]. The phosphorescence spectrum was assigned to the emission from neutral molecules, whereas the fluorescence was attributed to radical anions—negatively charged polarons.

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Solid *o*-, *m*-, and *p*-nitroanilines are weak semiconductors and give EPR signals [20]. Such signals grow up in the crystalline *m*-NA after the exposure to the near-IR (NIR) radiation corresponding to the second overtones of the –NH_2 stretching vibrations [21]. This radiation induces also the increase of the NIR absorption related to the conductivity. It has been proposed that the absorption is followed by the photoinduced proton transfers along the weak hydrogen bondings and lead to the formation of charge carriers with spins 1/2, called charged polarons, which on the molecular level correspond to the radical ions [21,22]. The computed value of the *m*-NA first order hyperpolarizability, β_{vec}, turned out to be larger for the radical anion than for the neutral molecule [19]. This last finding and the autocatalytic loop in creating charged polarons by the NIR radiation suggested that the open shell individuals are the intermediates responsible for the optical nonlinearity in the *m*-NA single crystals [19,21].

In the present work we measured the photoemission spectra of MNA and *p*-NA crystals and compared them with the *m*-NA crystal spectra [19]. For all the three crystals we recorded also the Stokes shifts between the absorption and emission onsets. Semi-empirical quantum chemical calculations were performed to facilitate the spectra interpretation. The aim of the study was to search for spectral differences between the three crystals and eventual manifestations of polarons.

2. Experimental and calculation methods

Single crystals of *p*-NA and *m*-NA were obtained from the zone refined material by the Bridgman method. The plates for measurements were obtained from bulky samples by cutting along the cleavage planes: (1 0 1) for *p*-NA and (0 1 0) for *m*-NA. Commercial MNA (Aldrich) was purified by the threefold vacuum sublimation. Thin crystalline plates (0 1 0) of MNA were grown by the evaporation from water–methanol (1:2) solutions [23]. Fluorescence and phosphorescence spectra were resolved by using a Parker-type disc-chopper phosphorimeter equipped with a liquid helium cryostat operating in the temperature range 5–300 K. Crystals at random orientation were excited by the 366 nm ($\nu_{\mathrm{exc}} \approx 27{,}300\,\mathrm{cm}^{-1}$) line, isolated by appropriate filters from the spectrum of an HBO200 mercury lamp or by the light of any wavelength within the range 300–500 nm obtained with a monochromator from the spectrum of a XBO75 xenon lamp. Emission was detected at right angle using a 25 cm Jarrel-Ash monochromator and an EMI 9659 photomultiplier, cooled to −20 °C, operating in the photon counting mode. Spectra were collected on a PC using a LightScan dual photon counter, which also controls the operation of the two monochromators. Decays of phosphorescence were accumulated with the aid of a Stanford Research SR430 multichannel scaler.

The semi-empirical modified INDO all-valence GRINDOL method [24] was used to calculate energies and oscillator strengths of electronic singlet–singlet transitions and electric dipole moments of the *p*-NA and MNA molecules. The energies of singlet–triplet and doublet–doublet transitions, for radical cations and radical anions, were calculated by the method described in Ref. [25].

3. Results and discussion

The calculated energies of singlet–singlet transitions, their oscillator strengths and the dipole moments of the excited states of the *p*-NA and MNA molecules in gas phase, as well as the absorption maxima observed in the crystals are presented in Tables 1 and 2, respectively. The calculated transitions energies of n–π^* nature are the same for both, *p*-NA and MNA molecules, while the energies of π–π^* transitions and the excited dipole moments differ only slightly (cf. data in Tables 1 and 2). The calculated values of π–π^* transition energies agree rather well with the corresponding band positions in crystals reported in Refs. [13,23]. In the case of MNA our results are also in agreement with the calculated ones for aggregates by Guillaume et al. [18]. The absorption spectra of gaseous *p*-NA [13] and MNA [1] as well as the spectra of *p*-NA and MNA in 1,4-dioxane solution are very similar [1]. The absorption spectra of all the three crystals are more complex than those of the compounds in gas phase, although in general they look similar.

Contrary to the absorption spectra, the emission spectra of considered crystals are different already at 5 K. The photoluminescence spectra of the *p*-NA and MNA single crystals at different temperatures are shown in Figs. 1 and 2, respectively. Fluorescence is the only emission observed in the *p*-NA crystals; the single broad band decreases with the temperature increase and disappears above 130 K (Fig. 1). The emission spectrum of the MNA crystal at 5 K (Fig. 2) is composed of both, fluorescence and phosphorescence. The phosphorescence spectrum has two maxima, at 17,200 and at 16,000 cm^{-1}, the decay time of this emission is about 150 ms. The fluorescence spectrum has the maxima at 21,500 and 20,300 cm^{-1}. With the temperature increase: the intensity of phosphorescence dramatically decreases above 30 K; the intensity of fluorescence continues to

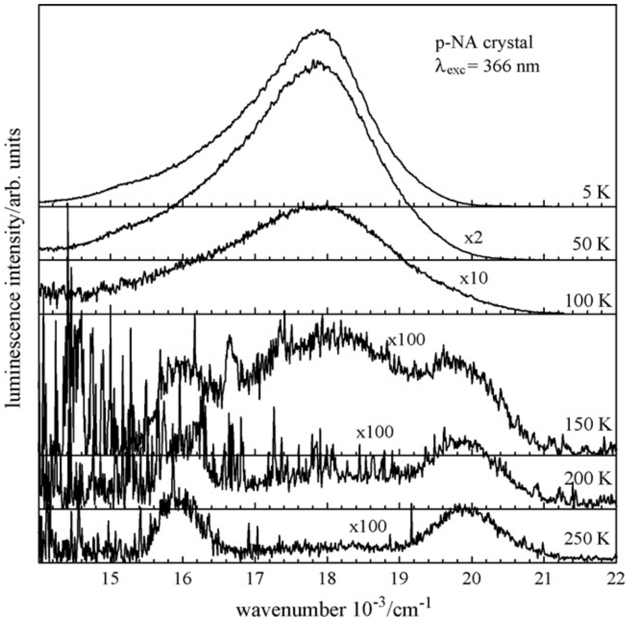

Fig. 1. Photoluminescence spectra of a *p*-NA single crystal at various temperatures.