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Excited State Two Photon Absorption of a Charge Transfer Radical Dimer in the Near Infrared

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Nonlinear transmission measurements of a solution of radical dimers of tetramethyl-tetrathiafulvalene, $(TMTTF^{+})_2$, recorded with 9 ns laser pulses at 1064 nm are reported and interpreted on the basis of a multiphoton absorption process. One finds that the process can be interpreted with a sequence of three photon absorption, the first being a one photon absorption related to the intermolecular charge transfer process characteristic of the dimers and the second a two photon absorption from the excited state created with the first process. A model calculation allows one to obtain the value of the two photon absorption cross section which is found to be several orders of magnitude larger than those usually found for two photon absorbing systems excited from the ground state. These results show the importance of an excited-state population for obtaining large nonlinear optical responses.

Multiphoton absorption processes are interesting for many applications for example in material science for optical limiters,[1,2,3] optical data storage,[4] 3D microfabrication,[5] optical switching,[6] and in the biological field for imaging with two-photon excited fluorescence.[7] Many molecules which have been considered for such applications show their multiphoton responses in the visible or first near-infrared spectral regions,[8] but many applications would benefit if the two photon activity would be shifted further in the infrared region at about 1000 nm where, for example, biological tissues are more transparent.

One of the main issues in multiphoton absorption research, in particular two-photon absorption (TPA) of molecules, is to find systems with large nonlinear absorption cross sections. Different types of molecules, related for example to a bis-styrylbenzene structure,[9] have been synthesized, but it was also predicted that if a system is in its excited states nonlinear responses much larger than if it is in its ground state can be found.[10,11] The reason is that molecules are much more polarizable in their excited states than in their ground state. We will show that, by using long pulses, such as nanosecond pulses, one can obtain a sufficient excited-state population to be able to observe exited state nonlinear optical responses and that these responses are very large as predicted.

Charge-transfer systems of omomolecular radicals are well-known systems in the field of organic conducting and superconducting materials. Molecules such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) have been used as building blocks of organic conducting crystals since the 70s[12] and derivatives of TTF, like bis-ethylenedithio-tetrathiafulvalene (BEDT-TTF) in particular, have been studied since the 80s for obtaining molecular superconducting crystals.[13,14] The smallest units of molecular aggregation of these systems are dimers of radicals which are quite stable in solution and show peculiar absorptions in the near-infrared spectral region.[15] Here we will show how the optical response of radical dimers of tetramethyl-tetrathiafulvalene ($TMTTF^{+}$; see Figure 1) to nanosecond pulses is quite interesting in the near-infrared region where the tail of the charge transfer absorption is located. We will show in particular that the response of the system, at 1064 nm, can be interpreted on the basis of a two photon absorption from an excited state (ES-TPA), and as recalled above, we will find a large nonlinear response which is usually not found for two photon absorbers excited from the ground state. Preliminary results on the nonlinear transmission measurements of solution of TMTTF neutral molecule and of the monomer of the its radical cation at 532 nm were already presented.[16]

$(TMMTF)ClO_4$ has been obtained by oxidation of TMTTF as already reported.[17] UV−vis−NIR spectra have been recorded with a Cary5 spectrophotometer (Varian Instrument), and the nonlinear transmittance data were registered by using 9 ns pulses at 1064 nm of a Nd:YAG laser (Quantel YG980E) and a setup which allows the control of the pulse energies with a half waveplate and a polarizing cube beam splitter. Pulse by pulse energies were measured with a pyroelectric detector (Scientech SPHD025) and a calibrated photodiode. Measurements were obtained in open configuration, namely with a large area detector near to the sample (solid angle 0.1 sterad) to avoid the influence of nonlinear scattering and nonlinear refraction effects. Areas of the laser pulses on the sample were of the order 0.2 cm in diameter to minimize borderline effects. Cells with 0.2 cm optical path were used for the solutions.

It is well-known that radicals of the TTF series can be present in solution as isolated molecules or as dimers of radicals which show a characteristic band in the near-infrared spectral region related to a charge transfer between the two moieties.[15] Figure 2 shows the spectrum of the $TMTTF^{+}$ radicals in acetonitrile,

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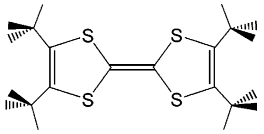

Figure 1. Molecular structure of tetramethyl-tetrathiafulvalene (TMT-TF).

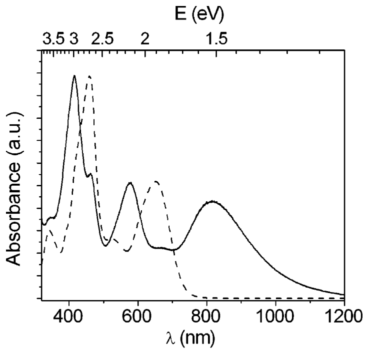

Figure 2. UV−vis−NIR spectra of TMTTF$^+$ radicals in DMSO (continuous line) where aggregation of molecules in the form of dimers is present and in acetonitrile (dashed line) where only the monomer is present. The band at 814 nm (1.52 eV) is the intermolecular charge-transfer band.

where the molecules are isolated, and in dimethyl sulfoxide (DMSO), where the molecules are associated in dimers.

Two bands related to intramolecular electronic excitations at 460 nm (2.70 eV) and 653 nm (1.90 eV) are present for the monomer spectrum. These bands are shifted to 416 nm (2.98 eV) and 577 nm (2.15 eV) in the dimer spectrum where a new band is also present at 814 nm (1.52 eV). This new band is characteristic of the associated molecules and has been identified as a charge-transfer excitation in which the final state corresponds to the two radical electrons present on one of the two molecules.[15] The presence of the charge-transfer excitation in the near-infrared spectral region is characteristic of the aggregated species of these radical systems and is the origin of the conducting and superconducting properties of crystals based on these types of molecules for which this band is shifted toward the very far-infrared.[13] Description of the charge-transfer band of these systems and of related new excitations of the infrared spectrum was obtained in the framework of the Hubbard model with electron correlation energies of the order of 1 eV and hopping parameters of the order of 0.1 eV.[18]

In the present paper, we are interested in the charge-transfer band as a source of electronic excitation in the near-infrared region that can be used in nonlinear optics.

Figure 3 shows the nonlinear transmission data of a 5.1 × 10^{-2} M (TMTTF)ClO$_4$ solution in DMSO by using 9 ns pulses at 1064 nm.

In Figure 3a, the transmission of the solution against input intensities (T/I_{in}) of the laser pulses is reported in a logarithmic scale and gives evidence in particular to the low intensity region where the nonlinear behavior starts to be present. Figure 3b reports the same experimental data but using the output intensities against input intensities ($I_{\mathrm{out}}/I_{\mathrm{in}}$) in a linear scale. In this case, one can easily observe, in particular, the high-intensity region, where multiphoton absorption can occur. The lower transmission in Figure 3a and the lower output intensities in Figure 3b, observed at high input intensities, show that a nonlinear absorption is occurring. We have also recorded the nonlinear transmission of a solution of the monomer in acetonitrile at 1064 nm, and we have not found any nonlinear response, showing that the nonlinear behavior is related to the presence of the dimers.

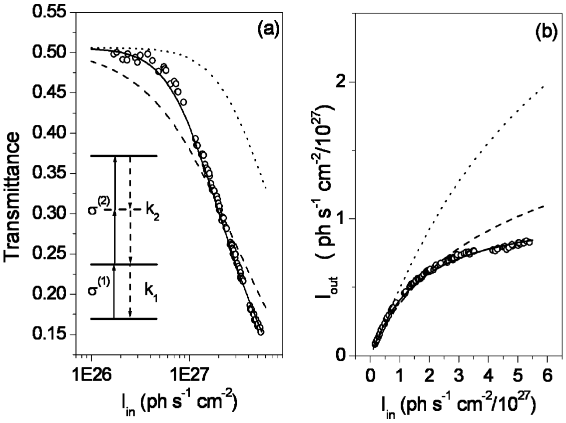

Figure 3. Nonlinear transmittance of a 5.1 × 10^{-2} M solution of TMTTF$^+$ radicals in DMSO with 9 ns pulses at 1064 nm. Model calculations for the 1+2 model (continuous line), for the 1+1 model (dashed line), and for the 1+2 model but with a 1 ps pulse (dotted line) (see text).

The interpretation of the experimental data can be obtained on the basis of a model for the dynamic of the excited states of the active species. Population dynamic is related to the diagonal elements of the more complete time dependent density matrix description of the interaction between light and matter. In this case, the diagonal elements are sufficient for the description of the process since coherent effects are not present using pulses with a long time duration with respect to the characteristic times of the molecular processes.[19,20]

At 1064 nm, there is a weak absorption due to the tail of the charge transfer band and, therefore, we have to consider that the first optical process is an absorption of a one photon from the ground state to the charge transfer excited state which is a process related to the first order optical susceptibility, usually 1 order of magnitude larger than higher optical susceptibilities. This absorption, however, accounts for the linear transmission of the sample. For the nonlinear behavior starting at about 5.0 × 10^{26} ph cm^{-2} s^{-1}, one has to consider other optical absorptions starting from the first excited state. The most simple processes one can consider are a one photon or a two photon absorption from this state.

In Figure 3 is reported (dashed line) the best result of a calculation[19] in which a one photon excitation from the excited state is considered (1+1 model). One can see that the fitting of the experimental data is very poor. This can be observed both in the T/I_{in}, at low intensities, and in the $I_{\mathrm{out}}/I_{\mathrm{in}}$, at high intensities, curves. In the same figures the result of the model calculation for a one photon excitation from the ground state and of a two photon excitation from the excited state (1+2 model) (continuous line) is also reported. In this case, the fitting is very satisfactory both in the low and in the high intensity regions. The fitting needs two parameters, namely the excited-state two photon absorption (ES-TPA) cross section ($\sigma_{\mathrm{ex}}^{(2)}$) and the relaxation constant for the intermediate first excited state (k_1). Another parameter of the model, namely the cross section for the one-photon excitation from the ground state ($\sigma^{(1)}$) is experimentally obtained from the linear spectrum whereas the relaxation from the highest final state (k_2) can be considered to be very fast, in the subpicosecond time scale. The inset in Figure 3 shows the energy levels scheme of the model. The best fitting with the 1+2 model has been obtained with $\sigma^{(1)} = 2.27 \times 10^{-19}$ cm^2, $\sigma_{ex}^{(2)} = 2.12 \times 10^{-43}$ cm^4 s ph^{-1} mol^{-1}, $k_1 = 1.5 \times 10^{11}$

s^{-1}, $k_2 = 8.0 \times 10^{12}$ s^{-1}. The result that the relaxation time from the first excited state ($k_1{}^{-1}$) is of the order of picoseconds (6.6×10^{-12} s) is consistent with the results of pump and probe measurements using nanosecond pulses which do not show any transient absorption in the nanosecond to the microsecond time scales. Pump and probe measurements with shorter pulses will give more information on this relaxation process. The value of $\sigma_{ex}^{(2)}$ shows that a very large nonlinear response is found for this process which starts from an excited state. The value of $\sigma_{ex}^{(2)}$ is, in fact, orders of magnitude larger than those observed for molecules excited from their ground states which are of the order, in the best cases, of 10^{-47} cm^4 s ph^{-1} mol^{-1} when it is taken into account that the two photon absorption occurs without involving excited-state populations.[8,21] The present result, on the other hand, depends on the possibility that a long pulse, such as that used in the experiment, generates an excited state population which is available to the photons of the same pulse for further excitations. This can be understood observing in Figure 3 the result of a calculation (dotted line) obtained by using the same parameters of the 1+2 model but considering a 1 ps pulse. In this case, the time duration of the laser pulse is of the order of the relaxation time of the first excited state so that a large enough population of this state is not obtained during the laser pulse and the fitting is no longer possible. Therefore, one concludes that the duration of the laser pulse is very important to be able to observe excited state non linear responses. Clearly also a small linear absorption is needed at the excitation frequency otherwise, as in the case of the monomer in acetonitrile, one is not able to obtain an excited-state population.

Laser pulses in the nanosecond time scale may have high energies but they usually have low intensities, with respect to picosecond or femtosecond pulses, to observe nonlinear optical effects and the possibility of recording nonlinear responses with nanosecond pulses can be traced back, many times, to excited-state responses as in the present case.[22] The model presented in this paper represents the simplest phenomenological understanding of the experimental data and a detailed analysis of the electronic molecular properties of the $TMTTF^+$ dimer will give more insight into the excited states dynamic which gives rise to the observed behavior as it was proposed for other systems.[23]

The search for new systems with large multiphoton absorption cross sections is usually focused on the synthesis of new types of molecules. However, using nonlinear properties of molecules in their excited states opens a new dimension of the materials in which high susceptibilities are obtained only for the time needed for the optical processes to occur. In the present paper, we have shown how a stable aggregation of $TMTTF^+$ radical dimers has a large ES-TPA in the infrared region.

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