

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/229368434>

Quantum-controlled color: Chirp- and polarization-sensitive two-photon photochromism of spiropyrans in the solid phase

ARTICLE *in* CHEMICAL PHYSICS LETTERS · NOVEMBER 2003

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2003.09.093

CITATIONS

17

READS

46

6 AUTHORS, INCLUDING:



Stanislav O Konorov

University of British Columbia - Vanco...

155 PUBLICATIONS 1,669 CITATIONS

SEE PROFILE



Ignac Bugar

TU Wien

55 PUBLICATIONS 380 CITATIONS

SEE PROFILE



Dusan Chorvat

International Laser Centre

142 PUBLICATIONS 1,213 CITATIONS

SEE PROFILE



Quantum-controlled color: chirp- and polarization-sensitive two-photon photochromism of spiropyrans in the solid phase

S.O. Konorov ^a, D.A. Sidorov-Biryukov ^b, I. Bugar ^c, D. Chorvat Jr. ^c,
D. Chorvat ^c, A.M. Zheltikov ^{a,b,*}

^a *Department of Physics, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119899 Moscow, Russia*

^b *International Laser Center, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119899 Moscow, Russia*

^c *International Laser Center, Ilkovičova 3, 81219 Bratislava, Slovak Republic*

Received 3 August 2003

Published online: 4 November 2003

Abstract

Phase and polarization control over photochromism in solid-state polymer materials doped with spiropyran compounds is demonstrated. Photochromism induced in spiropyrans by two-photon absorption of femtosecond pulses is shown to be sensitive to the initial chirp and polarization of these pulses. Enhancement of photochromism achieved by means of chirp and polarization control allows the yield of colored-form spiropyran to be increased by more than an order of magnitude.

© 2003 Published by Elsevier B.V.

1. Introduction

Photochromism is a light-induced reversible transformation in chemical species between two forms having different absorption spectra. The term photochromism, combining the Greek words phos (light) and chroma (color), is often routinely understood as light-induced change of color, well-known in every-day life due to photochromic glasses. Discovered back in the 19th century [1–4],

photochromism became a practical tool in the middle of the 20th century, when several new classes of photochromic materials have been demonstrated [5–7]. Applications of photochromism include self-developing photography, optical switching and filtering [8,9], three-dimensional optical data storage [10–13], and, since recently, reversible waveguide writing [14], microfabrication of photonic components [15,16], and engineering of photoswitchable biomaterials [17]. The advent of femtosecond lasers has opened a new phase in the understanding and applications of photochromism, allowing ultrafast, femtosecond-scale stages of photochromic reactions to be revealed [18–22]. Here we report phase and polarization

* Corresponding author. Fax: +7-95-9395174.

E-mail address: zheltikov@top.phys.msu.su (A.M. Zheltikov).

control over photochromism in solid-state polymer materials doped with spiropyran (SP) compounds. We demonstrate that photochromism induced by two-photon absorption (TPA) of femtosecond pulses is sensitive to their initial chirp and polarization and use this effect to enhance the photochromic reaction, increasing the yield of colored-form spiropyran by more than an order of magnitude.

2. Ultrafast dynamics of photochromic reactions: the key to photochromism control

The photochromic reaction in spiropyran compounds proceeds [23] through C–O bond cleavage (the upper inset in Fig. 1) and relaxation from a transient state (state X in Fig. 1) to a metastable merocyanine-form state (state B in Fig. 1). Until recently, the ultrafast dynamics of initial photochromic processes, including the

ultrafast C–O dissociation and formation of transient states, remained inaccessible to experimental investigations. The use of femtosecond pulses made it possible to study the ultrafast dynamics involved in photochromic processes and to measure the reaction rates for the initial steps of photochromic reactions [18–22].

The cleavage of C–O bonds in spiropyrans can be initiated by the absorption of one or several photons. Due to its nonlinear-optical nature, TPA is an intensity-dependent process, which strongly confines TPA-induced photochromic transformations to the focal area of laser beams [10–13,16]. As the pulse bandwidth increases with a decrease in the pulse duration, femtosecond pulses can be considered as wave packets in the frequency domain (Fig. 1). Because of their large spectral width, femtosecond pulses absorbed by a ground-state photochromic molecule through a one- or multiphoton process excite the whole group of vibrational levels, leading to the formation of a

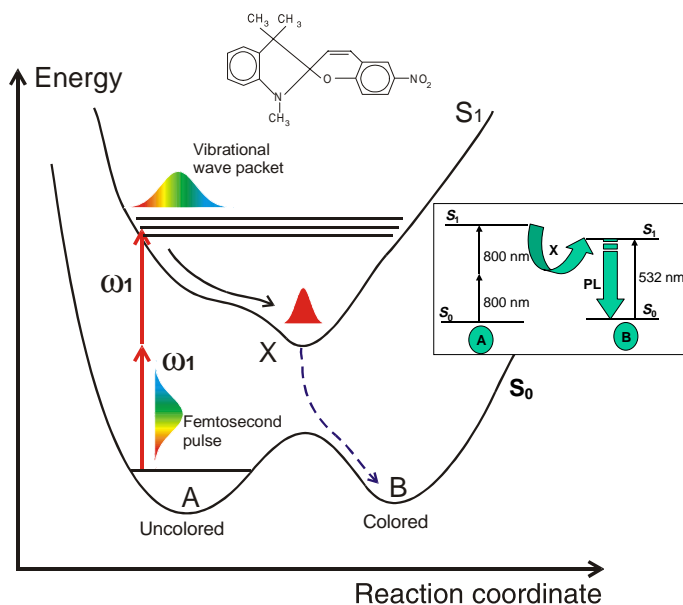


Fig. 1. Potential-curve diagram, illustrating the generic scenario of photochromic transformations in spiropyran: A, uncolored form of spiropyran; X, intermediate state; B, colored, merocyanine form of spiropyran. The reaction coordinate represents the dominant wave-packet motion direction in the reaction-coordinate space. TPA translates initially chirped laser pulses into chirped vibrational packets, which helps to synchronize individual oscillations in the target state. The upper inset shows the structure formula of spiropyran molecules. The lower inset sketches the initiation of the forward A \rightarrow B photochromic transformation through the TPA of 800-nm radiation and backward B \rightarrow A photochromic reaction through the one-photon absorption of 532-nm radiation.

vibrational wave packet in the electronically excited state (state S_1 in Fig. 1). This TPA-excited vibrational wave packet then evolves toward the transient state X. As shown by earlier time-resolved studies [20], this process of transient formation is at the heart of the ultrafast, femtosecond-scale phase of the photochromic reaction. The characteristic time of this process (the lifetime of the S_0 state in Fig. 1) depends on the environment of SP molecules and is typically estimated as 100–300 fs [20,22,24]. Time-resolved four-wave mixing measurements [24] indicate that the phase relaxation time for the S_1 state falls within the range of tens to hundreds of femtoseconds. Although the existence of the femtosecond stage of photochromism in SP molecules has been demonstrated by time-resolved measurements, the topology of the corresponding potential surfaces and, in particular, the character of transient-state potential still have to be explored. We have to rely, therefore, on a qualitative wave-packet interpretation of photochromism, which has been shown earlier [20,22] to provide useful insights into ultrafast physical and chemical processes behind the photochromism of SPs. As demonstrated by earlier work [22], form-B spiropyran is produced from the transient state X on a time scale on the order of a few picoseconds. The key idea of this work is to control the ultrafast, femtosecond-scale stage of the photochromic reactions by using the sensitivity of the TPA cross-section to the polarization state and the chirp of incident light pulses.

3. Experimental

The femtosecond laser system employed in our experiments (Fig. 2) consisted of a Ti:sapphire master oscillator, a stretcher, an amplifier, and a pulse compressor. The Ti:sapphire master oscillator was pumped by 4-W cw radiation of a diode-laser-pumped Nd:YVO₄ Verdi laser. The master oscillator generated laser pulses with a duration of 50–100 fs, a typical average output power on the order of 250 mW, and a pulse repetition rate of 100 MHz. Femtosecond pulses produced by the master oscillator were stretched up to 800 ps and launched into a multipass Ti:sapphire amplifier pumped with a nanosecond Nd:YAG laser with intracavity second-harmonic generation. Amplified 1-kHz picosecond pulses with an energy up to 300 μ J were then compressed to a duration of 100–130 fs in a single-grating pulse compressor. The chirp of laser pulses was controlled with a diffraction grating and was characterized with the spectral phase interferometry and autocorrelation techniques.

Our experiments were performed with PMMA samples doped with SP molecules (shown in the upper inset to Fig. 1). The concentration of SP in a $9 \times 10 \times 10$ mm³ sample was 1.6×10^{-2} mol/l. The uncolored form of SP molecules (form A) efficiently absorbs radiation with wavelengths shorter than 410 nm. The photochromic effect transforms A-form SP molecules into a colored form (form B), giving rise to the appearance of a broad absorption band in the visible region of the absorption spectrum of our SP/PMMA samples.

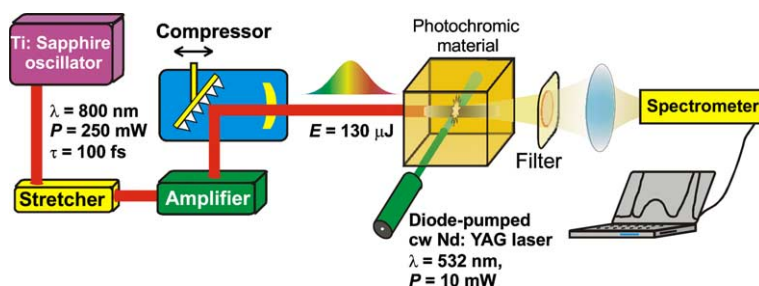


Fig. 2. Femtosecond laser setup. Laser pulses with a duration of 130 fs are used to TPA-induce a photochromic reaction in a 3D spiropyran/PMMA sample. The photochromic transformation is visualized by PL excited with 10-mW 532-nm second-harmonic radiation from an auxiliary diode-pumped cw Nd:YAG laser.

4. Results and discussion

Our 800-nm pump radiation is TPA-resonant with the transition between the ground electronic state S_0 of SP (form-A spiropyran) and the first excited electronic state S_1 . This transition triggers the photochromic reaction, resulting in the formation of merocyanine isomers (form-B spiropyran), visualized by characteristic changes in the spectrum of photoluminescence (PL) excited with 532-nm second-harmonic radiation from an auxiliary diode-pumped 10-mW cw Nd:YAG laser (Fig. 2). Radiation of this laser also stimulated reverse photochromic transformation (see the lower inset in Fig. 1), recovering form-A SP, thus preventing gradual pulse-to-pulse accumulation of form-B SP in the laser-irradiated area.

In a crude, but instructive approximation, the dynamics of $A \rightarrow B$ photochromic transformation in the presence of 800-nm Ti:sapphire-laser radiation and 532-nm second-harmonic radiation of a Nd:YAG laser, inducing forward and backward reactions (the lower inset in Fig. 1), is governed by the Eq. [12,13]

$$\frac{dN_B}{dt} = -\alpha p N_B W_2 + \beta q N_A W_1^2, \quad (1)$$

where α and β are the cross-sections of one- and two-photon absorption at the wavelengths of 532 and 800 nm, respectively; W_1 and W_2 are the flux densities of 800- and 532-nm photons, respectively; p and q are the relevant quantum yields; and N_A and N_B are the number densities of form-A and form-B SP molecules, with $N_A + N_B = N_0$, N_0 being the total number density of SP molecules. The upper inset in Fig. 3 illustrates a typical kinetics of the PL signal excited by 532-nm radiation in the SP/PMMA sample. As the Ti:sapphire laser is switched on at $t = 0$, TPA of 800-nm radiation initiates the $A \rightarrow B$ photochromic transformation. With the Ti:sapphire laser switched off at $t = 16$ s, the PL signal decays, indicating the recovery of form-A SP in the sample under the action of 532-nm radiation. The stationary level of the number density of form-B SP is given by $N_B^{\text{st}} = \beta q W_1^2 (\alpha p W_2 + \beta q W_1^2)^{-1} N_0$. This stationary regime was achieved in our experiments by adjusting the powers of 800- and 632-nm radiation.

Our first goal was to explore the influence of the chirp of Ti:sapphire laser pulses on the yield of form-B SP. Since the vibrational potential sensed by the wave packet in the electronically excited state S_1 is generally anharmonic, individual vibrations forming the excited-state wave packet reach the target transient state X at different moments of time. Initially chirped laser pulses, according to the general idea of quantum control with chirped pulses [25–27], help to synchronize individual oscillations in the target state. Fig. 3 shows the intensity of the PL signal from the Ti:sapphire-laser-irradiated area of an SP/PMMA sample (the PL spectrum is shown in the lower inset to Fig. 3) as a function of the initial chirp of Ti:sapphire laser pulses $\gamma = (1/2)(\partial^2 \theta / \partial \omega^2)$, where θ is the phase of the laser pulse. Negatively chirped pulses, as can be seen from this figure, enhance the generation of form-B SP relative to transform-limited or positively chirped pulses. The PL signal, which rapidly grows as the pulse chirp decreases from 0 down to -1000 fs^2 , becomes much less sensitive to the chirp for larger $|\gamma|$. This effect may be attributed to higher order phase aberrations of the pulse, which become noticeable for large $|\gamma|$. The data for negative chirps perfectly matched the positive-chirp data at zero chirp. The results of studies performed with chirped and transform-limited laser pulses having different energies and intensities agreed reasonably well with the predictions of Eq. (1), allowing the influence of the pulse chirp to be separated from the other factors.

The second knob in our quantum control approach is related to the polarization dependence of TPA, responsible for the formation of the excited-state wave packet in our system. Polarization dependence of the TPA cross-section is related to the tensor nature of this parameter, controlled by the spatial symmetry of the medium [13]. Angular momentum conservation dictates different selection rules for the absorption of two photons with different polarization-vector geometries, resulting in the excitation of physically different energy levels in the excited state of the system. Fig. 4 shows the PL signal from the TPA-excited area of the SP/PMMA sample as a function of the delay time between two linearly polarized 800-nm pump pulses with parallel (boxes) and perpendicular

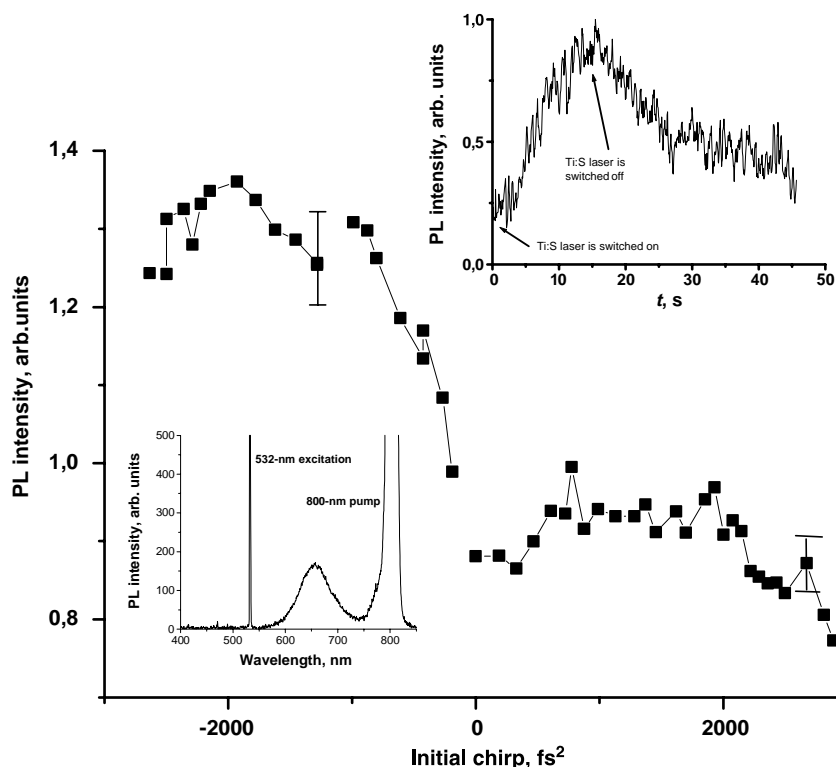


Fig. 3. The intensity of the PL signal excited with cw 532-nm laser radiation in the Ti:sapphire-laser-irradiated area of a spiropyran/PMMA sample as a function of the initial chirp of Ti:sapphire laser pulses. The upper inset displays the kinetics of the PL signal, visualizing the generation of form-B spiropyran in a polymer sample by 130-fs Ti:sapphire laser pulses and the recovery of form-A spiropyran under the action of 532-nm cw laser radiation. The lower inset shows the spectrum of PL excited with cw 532-nm laser radiation in the spiropyran/PMMA sample irradiated with 800-nm pump.

(circles) polarization vectors in a noncollinear beam-crossing geometry (shown in the upper inset in Fig. 4). The results of PL measurements are presented in Fig. 4 against the cross-correlation trace of the same pair of pulses measured in a 1-mm-thick BBO crystal (the dashed line), showing the negligibility of dispersion and pulse propagation effects in our experiments. The background in the τ dependence of the PL signal in Fig. 4 is due to the TPA photochromism induced by each of the pulses. The inset in Fig. 4 displays the dependence of the PL signal on the angle φ between the polarization vectors of linearly polarized Ti:sapphire laser pulses obtained upon the subtraction of the background, φ -independent component, related to the TPA photochromism induced by each of the laser pulses. The solid line in the inset to

Fig. 4 shows the approximation function $I(\varphi) \propto \eta \sin^2 \varphi + \cos^2 \varphi$, with $\eta = \text{Im}(\chi_{1122}^{(3)})/\text{Im}(\chi_{1111}^{(3)}) = 1/6$, where $\chi_{ijkl}^{(3)}$ is the cubic susceptibility tensor. Thus, linearly polarized femtosecond pulses with parallel polarization vectors produce form-B spiropyran in an SP/PMMA sample approximately six times more efficiently than linearly polarized pulses with perpendicular polarization vectors.

To check the nature of polarization and chirp control in our experiments, we directly measured TPA of Ti:sapphire laser radiation as a function of the chirp γ and the angle φ between the polarization vectors of Ti:sapphire laser pulses using the methodology of TPA studies described in detail elsewhere [12]. As the angle φ was changed from 0° to 90° , absorption of 800-nm pulses closely followed the dependence $D(\varphi) \propto \eta \sin^2 \varphi + \cos^2 \varphi$.

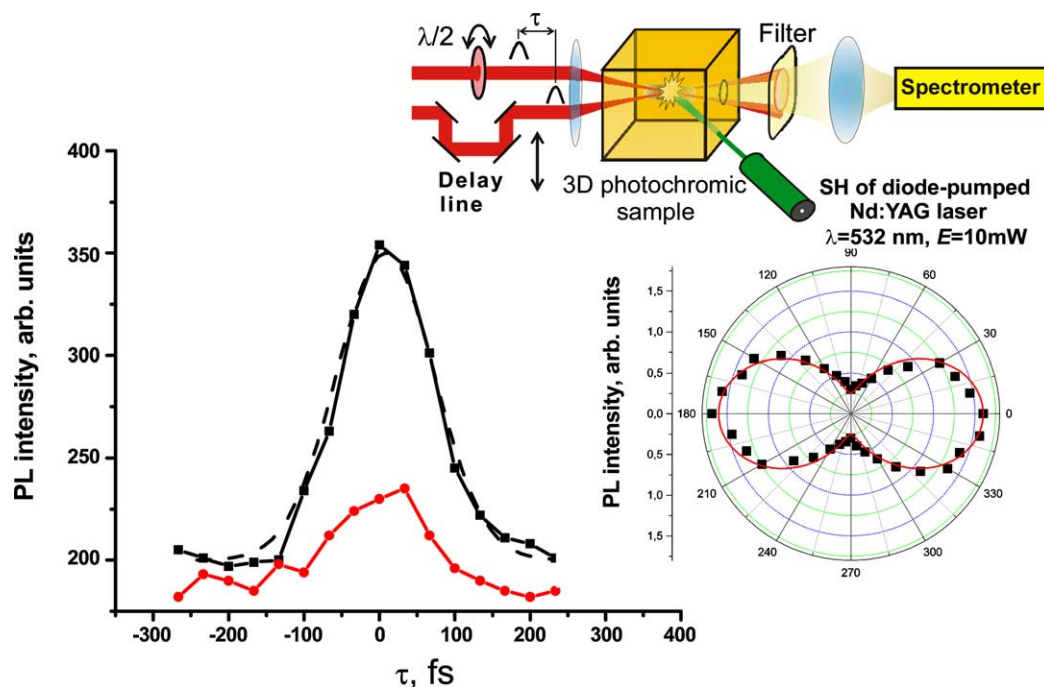


Fig. 4. The intensity of PL (solid lines) excited in the spiropyran/PMMA sample by 532-nm second-harmonic radiation of a diode-pumped cw Nd:YAG laser as a function of the delay time τ between the first and the second linearly polarized 800-nm pump pulses with parallel (boxes) and perpendicular (circles) polarization vectors in a noncollinear beam-crossing geometry (shown in the upper inset). The dashed line shows the cross-correlation trace of the same pair of pulses measured in a 1-mm-thick BBO crystal. The lower inset displays the dependence of the PL signal on the angle φ between the polarization vectors of linearly polarized Ti:sapphire laser pulses obtained upon the subtraction of the background, φ -independent component, related to the TPA photochromism induced by each of the laser pulses. The solid line in the lower inset shows the approximation function $I(\varphi) \propto \eta \sin^2 \varphi + \cos^2 \varphi$ with $\eta = 1/6$.

By contrast, chirp variation resulted in virtually no changes in the absorption of Ti:sapphire-laser pulses. These results suggest that the polarization control of photochromism in our experiments is due to the polarization control of TPA excitation process, related to the tensor properties of the relevant TPA cross-section (parameter β in Eq. (1)). This type of control is classified as quantum, since different polarization configurations of two absorbed photons allow quantum states with different total angular momenta to be accessed, in accordance with angular momentum conservation. The nature of chirp control is different, as indicated by the results of our measurements. The experimental data presented above can be self-consistently interpreted in terms of wavepacket focusing. Because of the lack of the information on the character of the potential surface

corresponding to the transient state X, it is, however, still not possible at the current stage to specify exactly the pathways whereby this control is realized.

5. Conclusion

The experiments presented above demonstrate the sensitivity of TPA-induced photochromism in solid-state polymer spiropyran materials to the initial chirp and polarization state of femtosecond pulses initiating the photochromic reaction. The choice of appropriate parameters on the chirp-polarization angle plane allowed us to vary the yield of spiropyran in the colored form within a broad dynamic range, including an order of magnitude enhancement of the photochromic reaction.

The use of TPA allowed strong absorption, typical of one-photon photochromism, to be avoided, giving an access to any point inside a 3D photochromic sample. Quantum-controlled photochromism, demonstrated in this work, offers new strategies for reversible 3D microfabrication using two-photon photochromism and suggests attractive solutions for the development of new photonic, telecommunication, biotechnological, and optical-memory components based on photochromic materials. The demonstration of quantum control of photochromism with chirped femtosecond pulses, on the other hand, opens new avenues for the extension of optimal-control approaches [27–33] to solid-state photochromic samples and global optimization of the chirp, shape, and polarization of ultrashort laser pulses used to initiate and steer photochromic reactions.

Acknowledgements

We are grateful to N.T. Sokolyuk for providing us with spiropyran samples and to J. Kovač Jr. for his help in experimental work. We also acknowledge fruitful discussions with A.B. Fedotov and S.A. Magnitskii.

This study was supported in part by the President of Russian Federation Grant MD-42.2003.02, the Russian Foundation for Basic Research (projects nos. 03-02-16929 and 02-02-17098), and the Volkswagen Foundation (project I/76 869).

References

- [1] J. Fritzsche, *Comptes Rendus Acad. Sci. Paris* 69 (1867) 1035.
- [2] E. ter Meer, *Ann. Chem.* 181 (1876) 1.
- [3] T.L. Phipson, *Chem. News* 43 (1881) 283.
- [4] W. Markwald, *Z. Phys. Chem.* 30 (1899) 140.
- [5] Y. Hirshberg, *Compt. Rend. Acad. Sci. Paris* 231 (1950) 903.
- [6] E. Fischer, Y. Hirshberg, *J. Chem. Soc.* (1952) 4522.
- [7] Y. Hirshberg, *J. Amer. Chem. Soc.* 78 (1956) 2304.
- [8] G.H. Brown (Ed.), *Photochromism*, Wiley, New York, 1971.
- [9] H. Bouas-Laurent, H. Dürr, *Pure Appl. Chem.* 73 (2001) 639.
- [10] D.A. Parthenopoulos, P.M. Rentzepis, *Science* 245 (1989) 843.
- [11] S. Hunter, F. Kiamilev, S. Esener, D.A. Parthenopoulos, P.M. Rentzepis, *Appl. Opt.* 29 (1990) 2058.
- [12] D.A. Akimov, A.M. Zheltikov, N.I. Koroteev, S.A. Magnitskii, A.N. Naumov, D.A. Sidorov-Biryukov, A.B. Fedotov, *Quantum Electron.* 26 (1996) 848.
- [13] D.A. Akimov, N.I. Koroteev, S.A. Magnitskii, A.N. Naumov, D.A. Sidorov-Biryukov, A.B. Fedotov, A.M. Zheltikov, *Jpn. J. Appl. Phys.* 36 (1997) 426.
- [14] S. Lecomte, U. Gubler, M. Jäger, Ch. Bosshard, G. Montemezzani, P. Günter, L. Gobbi, F. Diederich, *Appl. Phys. Lett.* 77 (2000) 921.
- [15] F. Ebisawa, M. Hoshino, K. Sukegawa, *Appl. Phys. Lett.* 65 (1994) 2919.
- [16] S.O. Konorov, A.B. Fedotov, A.M. Zheltikov, *Appl. Phys. B* 76 (2003) 707.
- [17] I. Wilner, *Acc. Chem. Res.* 30 (1997) 347.
- [18] N.P. Ernstig, B. Dick, Th. Arthen-Engeland, *J. Phys. Chem.* 95 (1991) 5502.
- [19] N. Tamai, H. Masuhara, *Chem. Phys. Lett.* 191 (1992) 189.
- [20] J.Z. Zhang, B.J. Schwartz, J.C. King, C.B. Harris, *J. Am. Chem. Soc.* 114 (1992) 10921.
- [21] N. Tamai, H. Miyasaka, *Chem. Rev.* 100 (2000) 1875.
- [22] S.A. Antipin, A.N. Petrukhin, F.E. Gostev, V.S. Marevtsev, A.A. Titov, V.A. Barachevsky, Yu.P. Strokach, O.M. Sarkisov, *Chem. Phys. Lett.* 331 (2000) 378.
- [23] T. Nakabayashi, N. Nishi, H. Sakuragi, *Sci. Prog.* 84 (2001) 137.
- [24] S.O. Konorov, D.A. Sidorov-Biryukov, I. Bugar, D. Chorvat Jr., D. Chorvat, A.M. Zheltikov, *Chem. Phys. Lett.* in press.
- [25] B. Kohler, V.V. Yakovlev, J. Che, J.L. Krause, M. Messina, K.R. Wilson, N. Schwenter, R.M. Whitnell, Y.J. Yan, *Phys. Rev. Lett.* 74 (1995) 3360.
- [26] C.J. Bardeen, Q. Wang, C.V. Shank, *Phys. Rev. Lett.* 75 (1995) 3410.
- [27] A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber, *Science* 282 (1998) 919.
- [28] R.S. Judson, H. Rabitz, *Phys. Rev. Lett.* 68 (1992) 1500.
- [29] H. Rabitz, R. deVivie-Riedle, M. Motzkus, K.-L. Kompa, *Science* 288 (2000) 824.
- [30] W. Kiefer (Ed.), *Femtosecond Coherent Raman Spectroscopy*, *J. Raman Spectros.* 31 (1/2) (2000) (special issue).
- [31] D. Zeidler, S. Frey, K.-L. Kompa, M. Motzkus, *Phys. Rev. A* 64 (2001) 023420.
- [32] J.L. Herek, W. Wohlleben, R.J. Cogdell, D. Zeidler, M. Motzkus, *Nature* 417 (2002) 533.
- [33] D. Zeidler, S. Frey, W. Wohlleben, M. Motzkus, F. Busch, T. Chen, W. Kiefer, A. Materny, *J. Chem. Phys.* 116 (2002) 5231.