

Coherent phase control of resonance-mediated two-photon absorption in rare-earth ions

Shian Zhang, Chenhui Lu, Tianqing Jia, Jianrong Qiu, and Zhenrong Sun

Citation: [Applied Physics Letters](#) **103**, 194104 (2013); doi: 10.1063/1.4830224

View online: <http://dx.doi.org/10.1063/1.4830224>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/103/19?ver=pdfcov>

Published by the [AIP Publishing](#)



Goodfellow

metals • ceramics • polymers
composites • compounds • glasses

Save 5% • Buy online
70,000 products • Fast shipping

Coherent phase control of resonance-mediated two-photon absorption in rare-earth ions

Shian Zhang,^{1,a)} Chenhui Lu,¹ Tianqing Jia,¹ Jianrong Qiu,² and Zhenrong Sun^{1,b)}

¹State Key Laboratory of Precision Spectroscopy and Department of Physics, East China Normal University, Shanghai 200062, People's Republic of China

²State Key Laboratory of Luminescent Materials and Devices and Institute of Optical Communication Materials, South China University of Technology, Wushan Road 381, Guangzhou 510640, People's Republic of China

(Received 4 August 2013; accepted 25 October 2013; published online 8 November 2013)

We theoretically and experimentally demonstrate the quantum coherent control of the resonance-mediated two-photon absorption in rare-earth ions by the phase-shaped femtosecond laser pulse. Our theoretical results show that the resonance-mediated two-photon absorption can be effectively controlled, but the control efficiency depends on the laser repetition rate in real experiment due to the long lifetime and the short decoherence time of the excited state, and the larger laser repetition rate yields the lower control efficiency. These theoretical results are experimentally confirmed in glass sample doped with Er³⁺ by utilizing the femtosecond lasers with low repetition rate of 1 kHz and high repetition rate of 80 MHz. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4830224>]

Recently, upconversion (UC) fluorescence has attracted much attention because of its ability to convert low frequency radiation to high frequency via two-photon or multiphoton absorption process^{1–3} and has been widely applied in various fields, including light-emitting diodes,⁴ laser sources,^{5,6} fiber optic communications,^{7,8} color displays,^{9–12} and biolabels.^{13–15} In particular, the UC fluorescence in rare-earth-ion doped nanocrystals can offer an attractive fluorescent labeling technique without many of the constraints associated with organic fluorophores and quantum dots.^{16,17} This UC technique usually utilizes near infrared (NIR) excitation rather than ultraviolet (UV) excitation and therefore can significantly minimize background autofluorescence, photobleaching, and photodamage. In addition, this technique has higher spatial resolution and longer sample penetration depth than that obtained by UV excitation.¹⁸ Consequently, these advantages can greatly simplify the detection scheme and improve the sensitivity and resolution.

The ability to effectively control the UC emission of the rare-earth ions is very important for their further applications. In this letter, we propose a femtosecond pulse shaping technique to control the multiphoton absorption or UC fluorescence in the rare-earth ions. This femtosecond pulse shaping technique has proven to be a well-established method to control various nonlinear optical processes in atomic and molecular systems,^{19–29} such as two-photon or multiphoton absorption,^{19–21} stimulated Raman scattering,^{22–24} harmonic order generation,²⁵ molecular alignment and orientation,^{26,27} and photoionization and photodissociation.^{28,29} We theoretically show that the resonance-mediated two-photon absorption in rare-earth ions can be effectively controlled by varying the laser spectral phase, but the control efficiency is correlated with the laser repetition rate in real experiment due to the long lifetime and the short decoherence time of

the excited state, and the lower control efficiency is obtained for the larger laser repetition rate. We experimentally confirm these theoretical predictions in the glass sample doped with Er³⁺ by applying different femtosecond lasers with low repetition rate of 1 kHz and high repetition rate of 80 MHz.

In the quantum system with broad absorption line, the multiphoton absorption is proportional to a sum of each individual transition. Based on the theoretical model of the atom system with narrow absorption line limit,²⁰ the resonance-mediated two-photon transition probability $S_f^{(1+1)}$ in rare-earth ions induced by a weak femtosecond laser field $E(t)$ can be approximated as

$$S_f^{(1+1)} \propto \int_{-\infty}^{+\infty} A(\omega_f) \left| \int_{-\infty}^{+\infty} A(\omega_i) \int_{-\infty}^{+\infty} E(t_1) \exp[i(\omega_f - \omega_i)t_1] \times \int_{-\infty}^{t_1} E(t_2) \exp(i\omega_i t_2) dt_2 dt_1 d\omega_i \right|^2 d\omega_f, \quad (1)$$

where ω_i and ω_f are the resonant frequencies of the immediate state $|i\rangle$ and final state $|f\rangle$, and $A(\omega_i)$ and $A(\omega_f)$ are the absorption line-shape function in the states $|i\rangle$ and $|f\rangle$. By transforming Eq. (1) into the frequency domain, $S_f^{(1+1)}$ can be further written as

$$S_f^{(1+1)} \propto \int_{-\infty}^{+\infty} A(\omega_f) \left| i\pi \int_{-\infty}^{+\infty} A(\omega_i) E(\omega_f - \omega_i) E(\omega_i) d\omega_i + \oint \int_{-\infty}^{+\infty} d\omega E(\omega_f - \omega) E(\omega) / (\omega_i - \omega) \right|^2 d\omega_f, \quad (2)$$

where $E(\omega)$ is the Fourier transform of $E(t)$ with $E(\omega) = E_0(\omega) \exp(i\Phi(\omega))$, and $E_0(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and phase, respectively. The first term in Eq. (2) is the on-resonant term that interferes all on-resonant two-photon excitation pathways with the frequencies of ω_i and $\omega_f - \omega_i$ while the second term is the near-resonant term that interferes all other near-resonant two-photon excitation

^{a)}Email: sazhang@phy.ecnu.edu.cn. Tel.: +86-21-62233210.

^{b)}Email: zrsun@phy.ecnu.edu.cn. Tel.: +86-21-62233210.

pathways with the frequencies of ω and $\omega_f - \omega$. The on-resonant term is excluded from the near-resonant term by Cauchy's principal value operator \wp . In rare-earth ions, the absorption bandwidth is usually relative large, and thus the near-resonant contributions in Eq. (2) can be negligible. Moreover, the excited state lifetime is usually very long in the range of microseconds, and so the resonance-mediated two-photon absorption process can be excited by multiple laser pulses that depend on the laser repetition rate in real experiment. Thus, $S_f^{(1+1)}$ can be simplified as

$$S_f^{(1+1)} \propto \sum_{m=1}^{R(\tau/T_d)} \sum_{n=m}^{R(\tau/T_d)} \int_{-\infty}^{+\infty} A(\omega_f) \times \left| \int_{-\infty}^{+\infty} A(\omega_i) E_n(\omega_f - \omega_i) E_m(\omega_i) d\omega_i \right|^2 d\omega_f, \quad (3)$$

where τ is the excited state lifetime, and T_d is the laser pulse separation with $T_d=1/f_L$, where f_L is the laser repetition rate. The symbol $R(\tau/T_d)$ indicates an upward rounded number. The decoherence time of the excite state in the rare-earth ions is usually in the range of picoseconds while the minimal laser pulse separation in real experiment is in the range of nanoseconds, corresponding to the laser repetition rate of MHz, and thus the resonance-mediated two-photon absorption process induced by two different laser pulses can be considered as two individual single-photon

absorption processes. Consequently, $S_f^{(1+1)}$ can be further written as

$$S_f^{(1+1)} \propto \sum_{m=1}^{R(\tau/T_d)} \int_{-\infty}^{+\infty} A(\omega_f) \times \left| \int_{-\infty}^{+\infty} A(\omega_i) E_m(\omega_f - \omega_i) E_m(\omega_i) d\omega_i \right|^2 d\omega_f + \sum_{m=1}^{R(\tau/T_d)} \sum_{n=m+1}^{R(\tau/T_d)} \int_{-\infty}^{+\infty} A(\omega_f) \int_{-\infty}^{+\infty} A(\omega_i) \times |E_n(\omega_f - \omega_i) E_m(\omega_i)|^2 d\omega_i d\omega_f. \quad (4)$$

The first term in Eq. (4) shows that the resonance-mediated two-photon absorption process takes place within the same laser pulse while the second term shows that this two-photon absorption process occurs by two different laser pulses. The different excitation pathways induced by the same laser pulse (i.e., P_{11} and P_{22}) and two different laser pulses (i.e., P_{12}) are presented in Fig. 1(b). It is easy to verify that the first term in Eq. (4) is maximal value for the transform-limited laser pulse and can be effectively suppressed by varying the laser spectral phase, but the second term is independent of the laser spectral phase and therefore is uncontrollable. Since the resonance-mediated two-photon absorption process in the rare-earth ions is controllable by the same laser pulse while is uncontrollable by two different

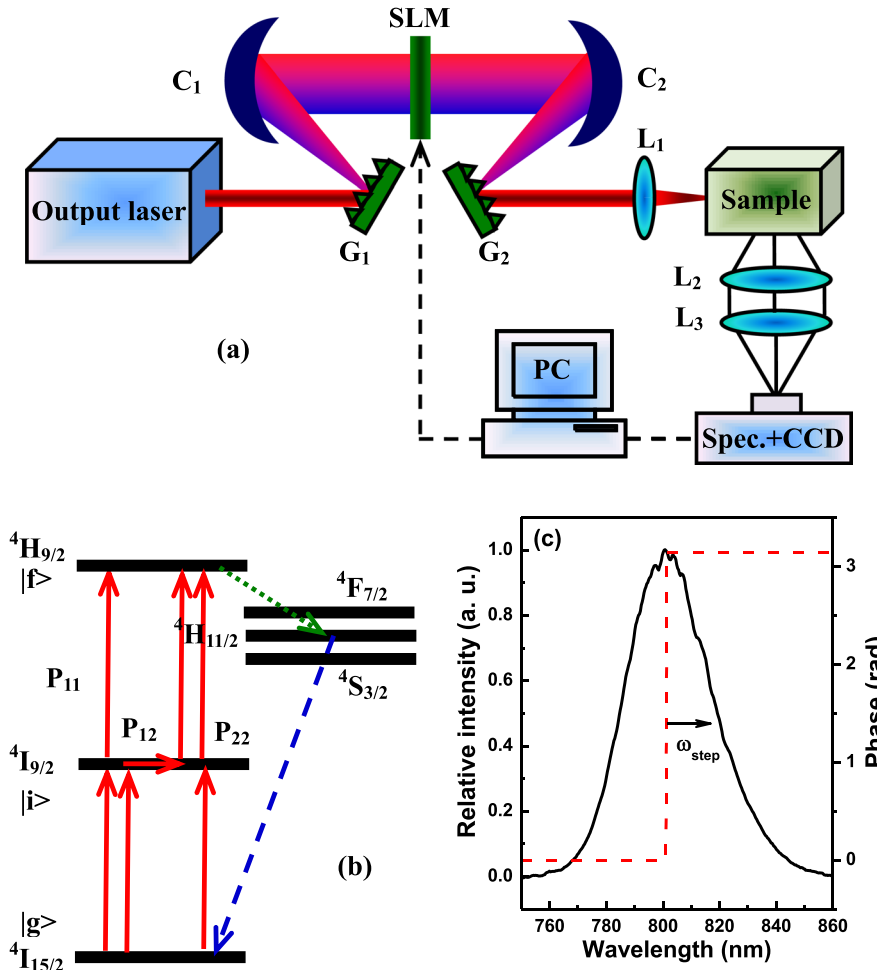


FIG. 1. (a) Schematic diagram of the experimental arrangement. The output laser pulse is shaped by a programmable 4f-configuration zero-dispersion pulse shaper combined with one-dimensional liquid-crystal spatial light modulator (SLM). (b) Energy level diagram of a resonance-mediated two-photon absorption and detected scheme in the glass sample $60\text{SiO}_2-20\text{Al}_2\text{O}_3-20\text{CaF}_2$ doped with Er^{3+} . (c) The laser spectrum is modulated by a π phase step modulation (red dashed line).

laser pulses, the laser repetition rate will affect the control efficiency of the resonance-mediated two-photon absorption, and the larger laser repetition rate yields the lower control efficiency.

To demonstrate the coherent phase control of the resonance-mediated two-photon absorption in rare-earth ions and the effect of the laser repetition rate on the control efficiency, we performed the experiment in the glass sample $60\text{SiO}_2-20\text{Al}_2\text{O}_3-20\text{CaF}_2$ doped with Er^{3+} , and the excitation and detection scheme is shown in Fig. 1(b), which includes the $^4\text{I}_{15/2}$ state as the ground state $|g\rangle$, the $^4\text{I}_{9/2}$ state as the intermediate state $|i\rangle$, and the $^4\text{H}_{9/2}$ state as the final state $|f\rangle$. The resonant frequency of the $^4\text{I}_{9/2}$ state is $\omega_i = \omega_{^4\text{I}_{9/2}} = 12\,563\text{ cm}^{-1}$, corresponding to the wavelength of 796 nm, and the resonant frequency of the $^4\text{H}_{9/2}$ state is $\omega_f = \omega_{^4\text{H}_{9/2}} = 24\,570\text{ cm}^{-1}$, corresponding to the wavelength of 407 nm. The population excited to the $^4\text{H}_{9/2}$ state spontaneously decays to the $^4\text{I}_{15/2}$ state through these lower $^4\text{F}_{7/2}$, $^4\text{H}_{11/2}$, and $^4\text{S}_{3/2}$ states. The total fluorescence intensity, including $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, serves as the relative measure for the $^4\text{H}_{9/2}$ state population.

The experimental arrangement is shown in Fig. 1(a). The output femtosecond laser pulse is shaped by a programmable 4f-configuration zero-dispersion pulse shaper, which is composed of a pair of diffraction gratings with 1200 lines/mm and a pair of concave mirror with 200-mm focal length. A one-dimensional liquid-crystal spatial light modulator (SLM-S320d, JENOPTIK) is placed at the Fourier plane of the pulse shaper and used as the updatable filter for the spectral phase modulation. The output shaped laser pulse is focused into the glass sample doped with Er^{3+} with a lens of 500-mm focal length. The fluorescence signal is collected perpendicularly and measured by a spectrometer with charge-coupled device (CCD). In our experiment, a π phase step modulation is used to control the resonance-mediated two-photon absorption in rare-earth ions, and the simple phase modulation is shown in Fig. 1(c), where ω_{step} is the phase step position. The π phase step modulation was considered as a well-established tool in quantum control of atom and molecular systems because it can create a constructive or destructive interference between different excitation pathways³⁰⁻³² and therefore has played a prominent role in the development of quantum control concepts and techniques.

We first use the femtosecond laser with low repetition rate to control the resonance-mediated two-photon absorption in the glass sample doped with Er^{3+} . A mode-locked Ti:sapphire femtosecond laser amplifier is used as excitation source with the central wavelength of 800 nm, the spectral bandwidth of 32 nm, and the repetition rate of 1 KHz. By comparing the excited state lifetime τ with the laser pulse separation T_d , one can obtain that $R(\tau/T_d) = 1$, that is to say, the resonance-mediated two-photon absorption process takes place within one laser pulse. Figure 2 shows the measured fluorescence intensity as function of the π phase step position ω_{step} , together with the theoretical curve calculated from Eq. (4). As can be seen, the fluorescence intensity can be effectively suppressed by $\sim 80\%$ but cannot be enhanced. This experimental observation is different from that in atom

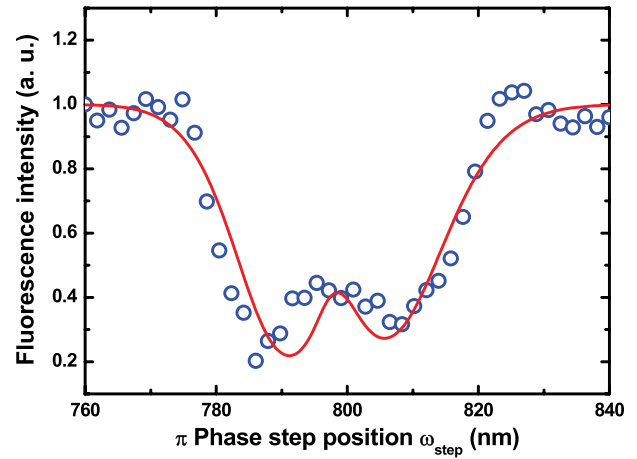


FIG. 2. The experimental (blue circles) and calculated (red line) normalized fluorescence intensity as a function of the π phase step position ω_{step} excited by a mode-locked Ti-sapphire femtosecond laser amplifier with the laser repetition rate of 1 kHz.

system,²⁰ where the resonance-mediated two-photon absorption can be completely suppressed and also effectively enhanced. The fundamental reason is that the broadband absorption in rare-earth ions will greatly suppress the constructive or destructive interference of these two-photon excitation pathways, as shown in Eq. (4). Since one laser pulse is excited in the resonance-mediated two-photon absorption process, only the first term in Eq. (4) contributes to the two-photon absorption while the second term does not because it results from the two different laser pulses, and thus the control efficiency of the two-photon fluorescence intensity is maximal value.

To emphasize the effect of the laser repetition rate on the control efficiency of the resonance-mediated two-photon absorption in rare-earth ions, we employ a mode-locked Ti-sapphire femtosecond laser oscillator as excitation source with the central wavelength of 800 nm, the spectral bandwidth of 35 nm, and the repetition rate of 80 MHz. Employing the same method as above, it can be seen that the resonance-mediated two-photon absorption process occurs by many laser pulses under the excitation using the femtosecond laser with high repetition rate. The measured fluorescence intensity as a function of the π phase step position ω_{step} is shown in Fig. 3, together with the theoretical curve. As expected, the control efficiency of the fluorescence intensity is greatly reduced by $\sim 8\%$. Since several laser pulses are simultaneously excited in the resonance-mediated two-photon absorption process, both the two terms in Eq. (4) contribute to the two-photon absorption, and the control efficiency of the two-photon fluorescence intensity will be reduced because the second term is uncontrollable. That is to say, the effect of the high repetition rate is to decrease the control efficiency.

In summary, we have theoretically and experimentally studied the coherent control of the resonance-mediated two-photon absorption in rare-earth ions by varying the laser spectral phase. Our theoretical results showed that the laser repetition rate in real experiment will affect the control efficiency due to the long lifetime and the short decoherence time of the excited state, and the larger laser repetition rate

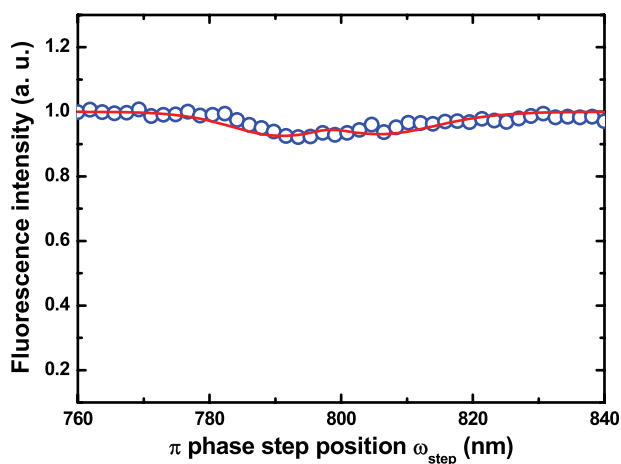


FIG. 3. The experimental (blue circles) and calculated (red line) normalized fluorescence intensity as a function of the π phase step position ω_{step} using a mode-locked Ti-sapphire femtosecond laser oscillator as excitation source with the laser repetition rate of 80 MHz.

will yield the lower control efficiency. We experimentally validated the effect of the laser repetition rate on the control efficiency of the resonance-mediated two-photon absorption in glass sample doped with Er^{3+} by utilizing the femtosecond lasers with low repetition rate of 1 kHz and high repetition rate of 80 MHz. Since the effect of the laser repetition rate on the coherent phase control of rare-earth ions is general behavior of any quantum system on resonance, our present work is very helpful for further understanding and controlling more complex resonance-mediated multiphoton absorption process in rare-earth ions.

This work was partly supported by National Natural Science Fund (Nos. 11004060, 11027403, and 51132004) and Shanghai Rising-Star Program (No. 12QA1400900).

¹F. Auzel, *Chem. Rev.* **104**, 139 (2004).

²F. Wang and X. Liu, *Chem. Soc. Rev.* **38**, 976 (2009).

³S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.* **39**, 189 (2010).

⁴S. Sivakumar, F. C. J. M. van Veggel, and M. Raudsepp, *J. Am. Chem. Soc.* **127**, 12464 (2005).

⁵R. Scheps, *Prog. Quantum Electron.* **20**, 271 (1996).

⁶E. Wintner, E. Sorokin, and I. T. Sorokina, *Laser Phys.* **11**, 1193 (2001).

⁷V. M. N. Tessler, M. Kazes, S. Kan, and U. Banin, *Science* **295**, 1506 (2002).

⁸P. Zhou, X. Wang, Y. Ma, H. Lü, and Z. J. Liu, *Laser Phys.* **22**, 1744 (2012).

⁹E. Downing, L. Hesselink, J. Ralston, and R. Macfarlane, *Science* **273**, 1185 (1996).

¹⁰G. Glaspell, J. Anderson, J. R. Wilkins, and M. S. El-Shall, *J. Phys. Chem. C* **112**, 11527 (2008).

¹¹Y. P. Li, J. H. Zhang, Y. S. Luo, X. Zhang, Z. D. Hao, and X. J. Wang, *J. Mater. Chem.* **21**, 2895 (2011).

¹²V. Mahalingam, F. Mangiarini, F. Vetrone, V. Venkatramu, M. Bettinelli, A. Speghini, and J. A. Capobianco, *J. Phys. Chem. C* **112**, 17745 (2008).

¹³F. van de Rijke, H. Zijlmans, S. Li, T. Vail, A. K. Raap, R. S. Niedbala, and H. J. Tanke, *Nat. Biotechnol.* **19**, 273 (2001).

¹⁴G. S. Yi, H. C. Lu, S. Y. Zhao, Y. Ge, W. J. Yang, D. P. Chen, and L. H. Guo, *Nano Lett.* **4**, 2191 (2004).

¹⁵L. Y. Wang, R. X. Yan, Z. Y. Huo, L. Wang, J. H. Zeng, H. Bao, X. Wang, Q. Peng, and Y. D. Li, *Angew. Chem., Int. Ed.* **44**, 6054 (2005).

¹⁶J. F. Suyver, A. Aebischer, D. Biner, P. Gerner, J. Grimm, S. Heer, K. W. Krämer, C. Reinhard, and H. U. Güdel, *Opt. Mater.* **27**, 1111 (2005).

¹⁷F. Wang, W. Tan, Y. Zhang, X. Fan, and M. Wang, *Nanotechnology* **17**, R1 (2006).

¹⁸K. König, *J. Microsc.* **200**, 83 (2000).

¹⁹D. Meshulach and Y. Silberberg, *Nature* **396**, 239 (1998).

²⁰N. Dudovich, B. Dayan, S. M. G. Faeder, and Y. Silberberg, *Phys. Rev. Lett.* **86**, 47 (2001).

²¹Z. Amitay, A. Gandman, L. Chuntunov, and L. Rybak, *Phys. Rev. Lett.* **100**, 193002 (2008).

²²D. Oron, N. Dudovich, D. Yelin, and Y. Silberberg, *Phys. Rev. Lett.* **88**, 063004 (2002).

²³D. Oron, N. Dudovich, and Y. Silberberg, *Phys. Rev. Lett.* **89**, 273001 (2002).

²⁴D. Oron, N. Dudovich, and Y. Silberberg, *Phys. Rev. Lett.* **90**, 213902 (2003).

²⁵R. Bartels, S. Backus, E. Zeek, L. Misoguti, G. Vdovin, I. P. Christov, M. M. Murnane, and H. C. Kapteyn, *Nature* **406**, 164 (2000).

²⁶O. Ghafur, A. Rouzée, A. Gijsbertsen, W. K. Siu, S. Stolte, and M. J. J. Vrakking, *Nat. Phys.* **5**, 289 (2009).

²⁷T. Suzuki, Y. Sugawara, S. Minemoto, and H. Sakai, *Phys. Rev. Lett.* **100**, 033603 (2008).

²⁸R. J. Levis, G. M. Menkiv, and H. Rabitz, *Science* **292**, 709 (2001).

²⁹A. Lindinger, C. Lupulescu, M. Plewicki, F. Vetter, A. Merli, S. M. Weber, and L. Wöste, *Phys. Rev. Lett.* **93**, 033001 (2004).

³⁰D. Meshulach and Y. Silberberg, *Phys. Rev. A* **60**, 1287 (1999).

³¹M. Wollenhaupt, T. Bayer, N. V. Vitanov, and T. Baumert, *Phys. Rev. A* **81**, 053422 (2010).

³²S. Zhang, H. Zhang, Y. Yang, T. Jia, Z. Wang, and Z. Sun, *J. Chem. Phys.* **132**, 094503 (2010).