Nonlinear Spectroscopy on a Single Quantum System: Two-Photon Absorption of a Single Molecule

Taras Plakhotnik,* Daniel Walser, Marco Pirotta, Alois Renn,
Urs P. Wild†

Two-photon fluorescence excitation spectra of single diphenyloctatetraene molecules trapped in an *n*-tetradecane matrix were measured at cryogenic temperatures. The purely electronic zero-phonon line (transition at 444 nanometers) of these single molecules with a width of about 60 megahertz was excited by a continuous-wave, single-mode laser at 888 nanometers. Even though the two-photon absorption cross section is extremely small, a high photon count rate and low background allowed nonlinear spectroscopy to be extended to the single-molecule level. This experiment also suggests the possibility of two-photon single-molecule scanning microscopy.

Optical experiments with single quantum systems (SQSs) have been steadily progressing. Single atoms in a beam, single ions in a Paul trap (*1*), single molecules on a surface (*2*), and single atoms in a magnetooptical trap (*3*) are promising systems that can be used to test quantum physics. Since 1989, optical spectroscopy of single molecules in solids (*4, 5*) has been achieved by several groups (*6*).

In all of these previous experiments, the SQS absorbed only one photon to undergo a transition from its ground state to the excited state, that is, the interaction of the SQS and the electromagnetic wave was linear. In our experiments, a nonlinear interaction between a single molecule (SM) and light occurs through simultaneous absorption of two photons, each carrying half of the energy needed for the optical transition.

Double quantum jumps in SQSs were treated theoretically in the 1930s (*7*). Such processes are fundamental for nonlinear optics, and here their direct observation is reported. Our experiments also open a way to two-photon scanning microscopy (*8*) on an SM level. This kind of microscopy will supplement SM optical (*9*) and near-field microscopy (*10*).

For SM spectroscopy, we used diphenyloctatetraene (DPOT) diluted in *n*-tetradecane (TD) (*11*). The DPOT was excited from its 1^1A_g ground state (S_0) to the lowest excited singlet state 2^1A_g (S_1) by two-photon absorption. The one-photon transition between these states is electric-dipole–forbidden by parity, but in a low-temperature matrix and a free supersonic jet (*12*), a weak one-photon emission due to coupling between 2^1A_g and nearby ^1B_u states can be observed. This can be seen in the low-resolution, one-photon excitation and luminescence spectra of DPOT in TD (Fig. 1), where a small peak at 444 nm corresponding to the one-photon transition to S_1 is observed. In a solid matrix, the observed lifetime T_1 of the S_1 state is about 6 ns, whereas the radiative lifetime T_{rad} is 66 ns (*13*). The blue luminescence (Fig. 1) was used in this work for SM detection.

We prepared the sample by dissolving a small amount of solid 1,8-diphenyl-1,3,5,7-octatetraene (Aldrich) in TD (Fluka) at a concentration of 2.5×10^{-5} M at room temperature. The solution was placed between two microscope cover-glass plates and was rapidly cooled to liquid He temperature to form a Shpol'skii matrix (*14*).

In the experiments (Fig. 2) a tunable single-mode continuous-wave Ti:sapphire laser (Coherent 899-29) was used for excitation at a wavelength of about 888 nm. The overall quantum yield of photon detection A_{tot} was approximately 1%; this yield included the solid angle of collection, optical losses, and the quantum efficiency of the photomultiplier (*15*). This A_{tot} was several times higher than under one-photon excitation, because the laser wavelength is twice the transition wavelength and the whole luminescence spectrum of DPOT including the strongest 0–0 line can be collected without interference from stray light. The fluorescence excitation spectra were recorded as a function of the laser wavelength. All measurements were performed in superfluid He at 1.7 K.

A two-photon excitation spectrum of the inhomogeneous band (Fig. 3) had a maximum intensity at about 888 nm and a linewidth of about 120 GHz. The average intensity of the band was proportional to the square of the laser intensity and was roughly proportional to the concentration of DPOT at room temperature (*16*). The peak position is in agreement with the value observed in the low-resolution spectra (Fig. 1), and the band shape is dominated by fluctuations called statistical fine structure (SFS) (*17*). This SFS is caused by fluctuations in the number of molecules per frequency interval in the excited volume and is reproducible from scan to scan (Fig. 4A).

The concentration of DPOT in the sam-

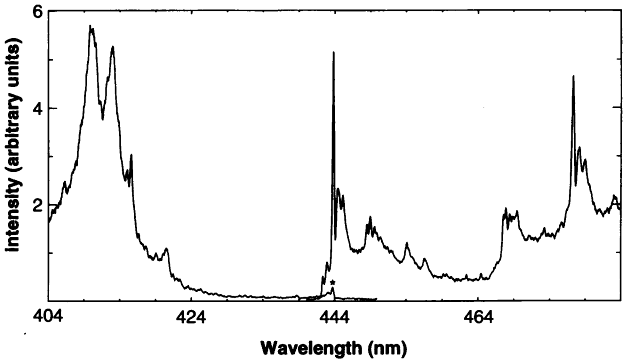

Fig. 1. Low-resolution, one-photon excitation (left) and luminescence (right) spectra of the DPOT in TD measured at 5 K. The strong broad line at 410 nm corresponds to the 0–0 zero-phonon line of the one-photon–allowed $1^1B_u \leftarrow 1^1A_g$ transition. The small peak at 444 nm is the 0–0 line of the $2^1A_g \leftarrow 1^1A_g$ transition (labeled by an asterisk). The broad band at about 445 nm in the luminescence spectrum is the phonon wing.

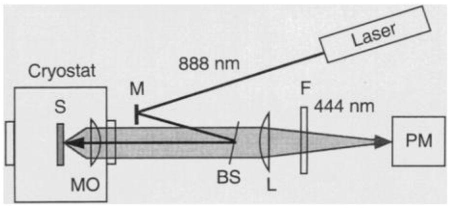

Fig. 2. Schematic diagram of the experimental setup for two-photon spectroscopy. A large portion (85%) of the laser intensity was reflected by a dichroic beam splitter (BS) and was focused onto the sample (S) by a microscope objective (MO) (Newport, achromatic, 60×, numerical aperture 0.85), which was immersed in liquid He. We achieved focusing by changing the distance to the sample, using a step motor also placed in the liquid He bath. The laser spot had a Gaussian shape. Its diameter on the sample surface was 3 μm. The fluorescence emitted by a single DPOT molecule was collected by the same MO and passed through the BS, which had a transmission of more than 80% at 444 nm. A lens (L) focused the fluorescence onto the photocathode of a photomultiplier (PM) (Hamamatsu, R4220P), whose quantum efficiency is about 20% at 444 nm and less than 10^{-6} at 888 nm. Laser radiation was additionally blocked by a glass filter (F) in front of the PM. When the mirror (M) is tilted, the spot position can be scanned over the sample.

Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland.

*Permanent address: Institute of Spectroscopy, 142092 Troizk, Russia.

†To whom correspondence should be addressed.

ple can be estimated from the SFS (*17*). The effective volume excited by two photons was 10^{-11} cm^3. Intensity fluctuations in the center of the inhomogeneous band were about 30%. Hence, the number of molecules in the excited volume per frequency interval, which is equal to the measured linewidth ($\Delta\nu_0$ = 30 MHz, see below), is approximately 10. This corresponds to a DPOT concentration of 7×10^{-6} M, in reasonable agreement with the concentration at room temperature (*16*).

A high-resolution scan measured in the red wing of the inhomogeneous band (Fig. 4B) shows three SM lines with a signal-to-background ratio of about 10. The background was proportional to the square of the laser power and was probably caused by nonresonant second harmonic generation in the substrate or sample itself. The second harmonic, which propagates in the direction of the excitation beam, was less than 4×10^4 photons per second. About 5% of these photons could be reflected from the sample surface and collected by the microscope objective.

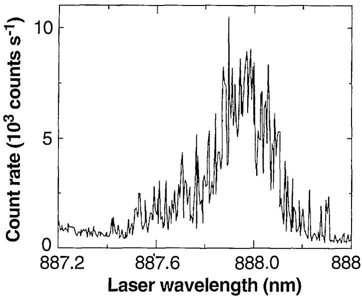

Fig. 3. Excitation scan over the inhomogeneously broadened two-photon absorption band. The concentration of DPOT was 2.5×10^{-5} M, and the laser intensity was about 4 MW cm^{-2}. The phonon wing is out of the scan range.

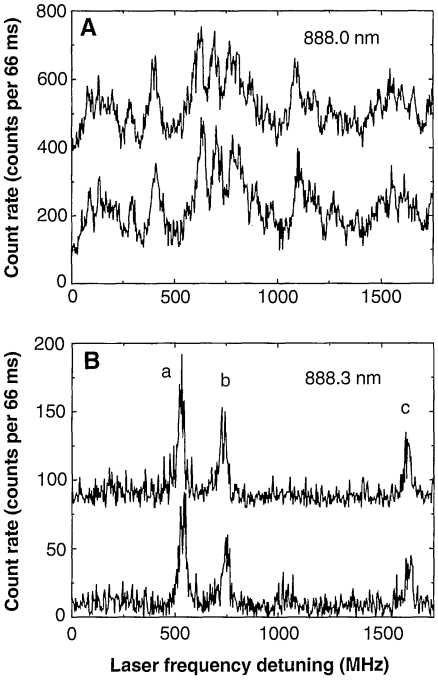

Fig. 4. (**A**) High-resolution scans in the center of the inhomogeneous band. The reproducibility of a structure in two traces shows SFS. (**B**) A high-resolution scan in the wing of the inhomogeneous band shows three SM lines labeled a, b, and c; the laser power was 2.5 MW cm^{-2}. On both (A) and (B), the upper trace is shifted vertically for clarity.

Some of the SMs showed spectral jumps, sudden disappearance of the signal after a few scans, a behavior observed in many experiments on SMs (*6*). Other SMs were very photostable, which allowed us to measure them at different excitation powers to determine the power dependence of their line intensity and linewidth (Fig. 5). At low power, the count rate R is proportional to the square of the laser intensity I; however, at higher power, R increases more slowly than I^2, indicating a saturation.

The linewidth varied only slightly upon increasing the laser intensity from 0.6 to 2 MW cm^{-2}, an indication that thermal heating was negligible in the low-power region. Moreover, even under light-induced heating, $\Delta\nu \times R$ should be proportional to I^2 (*18*). At the highest laser power, R is about one-fourth of the value extrapolated from low-power data (line $R \sim I^2$), whereas the line broadening is only 50% and does not compensate for the reduction in the line intensity. Hence, thermal heating cannot be responsible for the saturation and could only provide an unimportant contribution to the linewidth and the line-intensity dependencies.

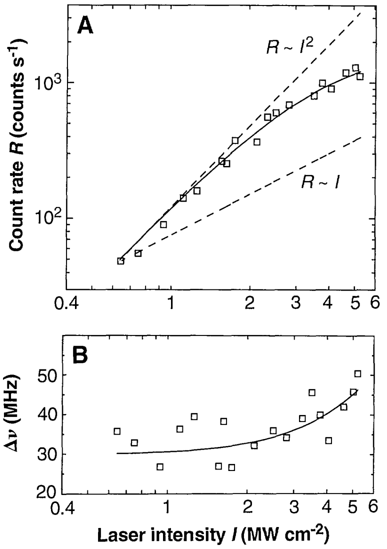

Fig. 5. Dependence of the count rate (**A**) and the measured linewidth $\Delta\nu$ (**B**) of molecule b (Fig. 4) on laser intensity. A least squares fit of Eqs. 6 and 7 to the experimental data is shown by solid lines. The dashed lines $R \sim I$ and $R \sim I^2$ are shown for comparison.

To explain the saturation, the triplet bottleneck has to be taken into account. According to simple rate equations, the count rate R in the center of an SM line and the measured linewidth $\Delta\nu$ are given by

$$R = \frac{A_{\text{tot}}}{2T_{\text{rad}}} \frac{K}{1 + \frac{(h\nu)^2 K}{2\sigma^{(2)} T_1 I^2}} \qquad (1)$$

and

$$\Delta\nu = \Delta\nu_0 \sqrt{1 + \frac{2\sigma^{(2)} T_1 I^2}{K (h\nu)^2}} \qquad (2)$$

where $h\nu$ is the photon energy, $K = 2/(2 + k_{23}/k_{31})$, k_{23} is the intersystem crossing rate, k_{21} is the total decay rate (including radiationless transitions and spontaneous emission) from the excited singlet directly to the ground state, $k_{21} + k_{23} = 1/T_1$, k_{31} is the total decay rate from the triplet to the ground state, $\Delta\nu_0$ is the low-power limit of the measured linewidth, and $\sigma^{(2)}$ is the so-called two-photon absorption "generalized cross section."

Equations 1 and 2 would be identical to the well-known equations describing one-photon excitation [see, for example, (*19*)], if $\sigma^{(2)} I/(h\nu)$ was replaced by σ.

It is assumed that the Lorentzian lineshape function is given by

$$g(\nu) \sim \frac{1}{(\nu_0 - \nu)^2 + \frac{\Delta\nu^2}{4}} \qquad (3)$$

where ν is the laser frequency and ν_0 is the center frequency of a SM line. If we introduce the high-power count rate

$$R_\infty = \frac{A_{\text{tot}} K}{2T_{\text{rad}}} \qquad (4)$$

and the saturation intensity

$$I_{\text{sat}} = h\nu \sqrt{\frac{K}{2\sigma^{(2)} T_1}} \qquad (5)$$

Eqs. 1 and 2 can be rewritten as

$$R = \frac{R_\infty}{1 + \frac{I_{\text{sat}}^2}{I^2}} \qquad (6)$$

and

$$\Delta\nu = \Delta\nu_0 \sqrt{1 + \frac{I^2}{I_{\text{sat}}^2}} \qquad (7)$$

At low power we get

$$R = \frac{A_{\text{tot}} T_1}{T_{\text{rad}}} \sigma^{(2)} \left(\frac{I}{h\nu}\right)^2 = \frac{R_\infty}{I_{\text{sat}}^2} I^2 \qquad (8)$$

We performed a least squares fit of Eqs. 6 and 7 to our experimental data (Fig. 5), in which R_∞, $\Delta\nu_0$, and I_{sat} were equal to 1900 counts s^{-1}, 30 MHz, and 4.1 MW cm^{-2}, respectively (*20*). In the case of two-photon absorption, the line-shape function $S(\nu)$ is proportional to $1/[(\Omega - 2\nu)^2 + (\Gamma/2)^2]$ (*21*), where Ω is the transition frequency, ν is the laser frequency, and Γ is the molecular linewidth. Hence, to get Γ, the experimentally measured value $\Delta\nu_0$ must be multiplied by a factor of 2. The molecular linewidth is more than twice the lifetime-limited value $1/(2\pi T_1)$. The difference may have been caused by spectral diffusion (*22*); further investigations are required to determine the origin of this difference. Spectral diffusion can also be responsible for fluctuations in the experimental values of $\Delta\nu$ (Fig. 5).

From Eq. 8 and the experimental data, it follows that $\sigma^{(2)} = 6 \times 10^{-45}$ cm^4 s (*23*). The parameters K and k_{31} can be estimated as well, because $K = 2R_\infty T_{\mathrm{rad}}/A_{\mathrm{tot}}$ and $k_{23} = 8 \times 10^5$ s^{-1} (*24*), giving $K = 2.5 \times 10^{-2}$ and $k_{31} = 1 \times 10^4$ s^{-1} (*20*). The value for k_{31} is in reasonable agreement with the triplet decay rate measured for shorter diphenylpolyenes [2.5×10^3 s^{-1} for diphenylhexatriene and 4.1×10^2 s^{-1} for diphenylbutadiene (*25*)].

From our observations we conclude that the recorded signal corresponds to the emission of DPOT molecules excited by two photons. In spite of recent achievements in SM spectroscopy, it was not clear at the beginning of this research if the two-photon excitation of an SM was feasible at all. The extremely low cross section of two-photon absorption, thermal heating under excitation by strong laser light, and low count rate as a result of saturation were anticipated obstacles for such experiments. The very low background under two-photon excitation made our experiment possible.

REFERENCES AND NOTES

1. For reviews, see: W. M. Itano, J. C. Bergquist, D. J. Wineland, *Science* **237**, 612 (1987); H. Walther, *Aust. J. Phys.* **46**, 37 (1993), and references therein.
2. E. Betzig and R. J. Chichester, *Science* **262**, 1422 (1993).
3. Z. Hu and H. J. Kimble, *Opt. Lett.* **19**, 1888 (1994).
4. W. E. Moerner and L. Kador, *Phys. Rev. Lett.* **62**, 2535 (1989).
5. M. Orrit and J. Bernard, *ibid.* **65**, 2716 (1990).
6. For the latest review, see: L. Kador, *Phys. Status Solidi B* **189**, 11 (1995).
7. M. Göppert-Mayer, *Ann. Phys.* **9**, 273 (1931).
8. R. M. Williams, D. W. Piston, W. W. Webb, *FASEB J.* **8**, 804 (1994); W. Denk, J. H. Strickler, W. W. Webb, *Science* **248**, 73 (1990).
9. F. Güttler, Th. Irngartinger, T. Plakhotnik, A. Renn, U. P. Wild, *Chem. Phys. Lett.* **217**, 393 (1994).
10. W. P. Ambrose, P. M. Goodwin, J. C. Martin, R. A. Keller, *Science* **265**, 364 (1994).
11. Chromophores of the octatetraene type have been thoroughly investigated [B. S. Hudson and B. E. Kohler, *J. Chem. Phys.* **59**, 4984 (1973); ______, K. Schulten, in *Excited States*, E. C. Lim, Ed. (Academic Press, New York, 1982), vol. 6, p. 1]. It was shown that the lowest singlet transition is of the $2^1A_g \leftarrow 1^1A_g$ type. Two-photon excitation inhomogeneously broadened spectra of octatetraene in *n*-octane have been recorded [M. F. Granville, G. R. Holtom, B. E. Kohler, *J. Chem. Phys.* **72**, 467 (1980)].
12. H. Petek *et al.*, *J. Chem. Phys.* **98**, 3777 (1993).
13. Cyclohexane solution, I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic Press, New York, ed. 2, 1971).
14. E. V. Shpol'skii, *Sov. Phys. Usp.* **6**, 411 (1963).
15. T. Plakhotnik, W. E. Moerner, V. Palm, U. P. Wild, *Opt. Commun.* **114**, 83 (1995).
16. The intensity of the inhomogeneous band varied by a factor of about 5 when the laser spot was moved from one place on the sample to another.
17. W. E. Moerner and T. P. Carter, *Phys. Rev. Lett.* **59**, 2705 (1987).
18. As no intensity redistribution between the zero-phonon line and the phonon wing was observed, interaction with phonons can cause only a dephasing. In this case thermal heating does not change the area of the zero-phonon line [K. K. Rebane, *Impurity Spectra of Solids* (Plenum, New York, 1970)].
19. W. P. Ambrose, Th. Basché, W. E. Moerner, *J. Chem. Phys.* **95**, 7150 (1991); H. de Vries and D. A. Wiersma, *ibid.* **72**, 1851 (1979).
20. On the basis of the measurement of a few molecules only, variations of the order of about 20% were observed in the low-power linewidth, the saturation intensity, and the high-power count rate. More statistics are needed to get the real distribution of these values.
21. F. H. M. Faisal, *Theory of Multiphoton Processes* (Plenum, New York, 1987), p. 49.
22. L. R. Narasimhan, D. W. Pack, M. D. Fayer, *Chem. Phys. Lett.* **152**, 287 (1988).
23. The value is about four orders of magnitude larger than that measured at room temperature [R. J. M. Anderson, G. R. Holtom, W. M. McClain, *J. Chem. Phys.* **70**, 4310 (1979)] because of dramatic line narrowing at low temperature.
24. R. Bensasson, E. J. Land, J. Lafferty, R. S. Sinclair, T. G. Truscott, *Chem. Phys. Lett.* **41**, 333 (1976).
25. G. Heinrich, G. Holzer, H. Blume, D. Schulte-Frohlinde, *Z. Naturforsch. Teil B* **25**, 496 (1970).
26. This work was supported by the Swiss National Science Foundation and by Eidgenössiche Technische Hochschule Zurich.

30 October 1995; accepted 4 January 1996

Are Single Molecular Wires Conducting?

L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar,
T. P. Burgin, L. Jones II, D. L. Allara,* J. M. Tour,* P. S. Weiss*

Molecular wire candidates inserted into "nonconducting" *n*-dodecanethiol self-assembled monolayers on Au{111} were probed by scanning tunneling microscopy (STM) and microwave frequency alternating current STM at high tunnel junction impedance (100 gigohms) to assess their electrical properties. The inserted conjugated molecules, which were 4,4′-di(phenylene-ethynylene)benzenethiolate derivatives, formed single molecular wires that extended from the Au{111} substrate to about 7 angstroms above and had very high conductivity as compared with that of the alkanethiolate.

Molecular wires (MWs) are among the key components in the emerging field of molecular electronics. In their simplest form, MWs can be viewed as conjugated molecules that form one-dimensional electronic conductors to interconnect such proposed molecular devices as single electron transistors, electron turnstiles, molecular switches, and chemical sensors (*1*). Although many MW candidates have been prepared (*2*), the conductivity of single MWs has not been demonstrated. This is due in part to the difficulty of individually connecting a single MW to probes. In this report, we describe how molecular self-assembly was used both to anchor an MW candidate to an electrode (the Au{111} substrate) and to dilute and isolate the MW candidates within a self-assembled monolayer (SAM) of *n*-dodecanethiol (DT). The second connection to the MW candidate was achieved via the probe tip of an STM or a tunable microwave frequency alternating current STM (ACSTM). The individual molecules can be observed in conventional STM images as well as by their microwave frequency electronic properties. The STM can then individually examine the inserted MW candidates and probe their electronic properties.

Bulk conductivity measurements of MW candidates include conduction paths along the molecule and percolation between the chains. Wu and Bein have grown isolated polyaniline molecules (*3*) and graphitic carbon (*4*) in zeolite matrices to eliminate interchain percolation and have demonstrated the molecules' conductivity using a microwave cavity perturbation technique at 2.63 GHz. Jones *et al.* (*5*) have made preliminary measurements using mechanical break junctions containing 1,4-benzenedithiol. Unfortunately, these tunnel junctions are ill defined in that it is difficult to know if the conducting channel is a single molecule or is even the molecule of interest. The STM and ACSTM are ideal for this study because they allow us to image the surface and locate isolated molecules, which are

---

L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, P. S. Weiss, Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA.
T. P. Burgin, L. Jones II, J. M. Tour, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA.
D. L. Allara, Departments of Chemistry and Materials Science, Pennsylvania State University, University Park, PA 16802, USA.

*To whom correspondence should be addressed.