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Formation and measurement of molecular quantum picostructures

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Using two laser pulses of femtosecond duration we excite a diatomic molecule (I_2) to a dissociative state where the wave function is localized around two internuclear separations. The structure of the wave function is controlled by the relative amplitude and the temporal separation of the exciting laser pulses. A delayed intense probe pulse measures the square of the wave function as a function of the internuclear separation $|\Psi(R)|^2$ by Coulomb exploding the molecule. We report a resolution of ~2 Å in the internuclear range ~6–15 Å. We discuss how intense femtosecond laser pulses provide a different approach to time-resolved photochemistry. [S1050-2947(97)50505-1]

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Manipulation and imaging of matter at the atomic and molecular level is presently a subject of tremendous interest and activity in physics, chemistry, and biology. In the condensed phase, the development of scanning probe microscopes has enabled imaging of the topography and electronic structure of surfaces of solids with atomic resolution, and individual atoms and molecules can be selected and manipulated [1,2]. In atomic physics, lasers are used, for example, to cool and trap isolated atoms [3] and to manipulate beams of atoms in a way analogous to manipulation of light by optics [4]. In femtosecond transition-state spectroscopy of molecules, femtosecond laser pulses are employed to initiate chemical reactions and to follow their evolution in real time [5].

Here we report that femtosecond lasers provide a tool for producing multipeaked molecular nuclear wave functions with adjustable amplitudes and separations between the peaks [6]. This is achieved using multiple femtosecond pulses to excite a molecule. In this way the molecule is placed in a coherent superposition of internuclear continuum states with controllable internuclear positions, amplitudes, and electronic phases. These molecular structures, which we call quantum picostructures, are time dependent by construction and they combine spatial and temporal control on the natural spatial (in angstroms) and time (in femtoseconds) scales of molecules. Furthermore, these structures may provide a means to modulate or control (e.g., through diffraction) light or matter waves on an ultrafast time scale [7].

We also demonstrate how the quantum picostructures can be measured. Time-resolved measurements must, of necessity, involve at least two photons—one to start the process of interest (pump-step) and one to probe the evolution of the process at later times (probe-step). In most studies of fast processes in molecules, atoms, or condensed media to date, only two photons are used. In this way, interpretation of the results has been kept as simple as possible, since lowest-order perturbation theory applies. Equally simple and intuitive models now exist for strong-field processes [8,9] in which a large number of photons is absorbed by atoms or molecules in gas phase. To describe atomic ionization in strong ultrashort fields, these models ignore all the resonant effects treating ionization as tunneling in a time-dependent electric field. Ignoring resonances is justified in high-order multiphoton processes, since all the levels are Stark shifted by the strong laser field; so resonances, if they are present, are so dynamic that they are hardly resonances at all [10]. If the laser field is perpendicular to the molecular axis the ionization is atomiclike [9,11].

Performing pump-probe experiments in the strong-field limit is almost unexplored, but has the potential to lead to completely new insight [11], since studies in this extreme have no partner in the frequency domain. In the present work we employ a strong field polarized perpendicularly to the internuclear axis in the probe step. We measure the position and shape of the quantum picostructures by rapidly stripping several electrons from the molecule and measuring the Coulomb energy released as kinetic energy of the resulting atomic ions [12]. The potential curves of molecular ions may deviate from Coulombic at small internuclear separation ($R<5$ Å for iodine) [13], therefore we restrict our measurements to large internuclear separations.

The experiment is illustrated in Fig. 1. First, the quantum picostructures are formed by exciting I_2 molecules from the ground state to the repulsive $A\,^3\Pi_u$ state with two 80-fs-long (full width at half maximum) laser pulses separated by ~310 fs. Second, the excited I_2 molecules dissociate with an internuclear speed of ~11.6 Å/ps. Third, the instantaneous shape of the picostructure is measured by Coulomb exploding the molecule with an intense 80-fs delayed pulse [12]. By recording the distribution of kinetic energies of the exploded ionic fragments and using Coulomb's law we can determine the structure of the square of the internuclear wave function [14].

The experiment is performed inside an ultrahigh-vacuum chamber where iodine molecules in a supersonic molecular beam (buffered with 1 atm of helium) are irradiated by the femtosecond pulses focused with an on-axis parabolic mirror ($f/2$). The kinetic energies of the ionic fragments are measured in a time-of-flight spectrometer [12,15] oriented perpendicular to the axis of the molecular beam and to the polarization and the direction of the laser beams. The pump and probe pulses are generated by sending the output from an

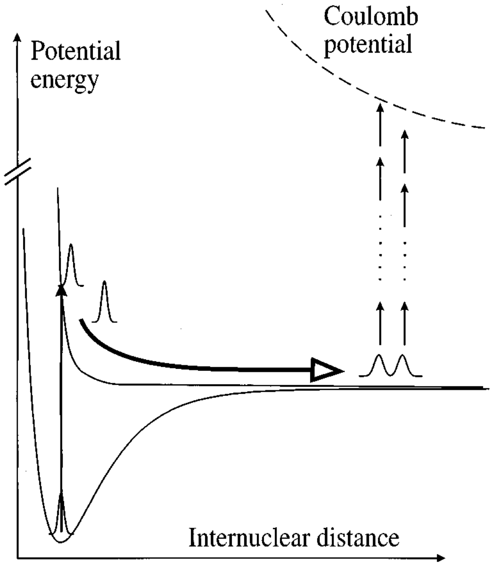

FIG. 1. Schematic of a few potential curves of I_2 illustrating the formation of the quantum picostructure and its subsequent projection by multiphoton ionization onto a repulsive Coulomb potential.

amplified femtosecond laser system (10 Hz, 250 μJ, 80 fs, 625 nm) through a Michelson arrangement [15]. A mirror in the ''probe arm'' is mounted on a motorized translation stage to control the delay. A 5-mm-thick crystalline quartz plate is inserted in the ''pump arm'' of the Michelson. The difference in the refractive index between the ordinary and the extraordinary axis of the birefringent crystal produces two femtosecond pulses separated by ~310 fs, as measured by cross correlation. A polarizer inserted after the Michelson ensures that the pump pulses and the probe pulse have the same polarization. In addition, the polarizer allows us to control the relative intensity of the two pump pulses simply by rotating the quartz plate. Finally, the quartz plate forces a well-defined phase relation between the two pulses, although it is not measured or exploited in this experiment.

In Fig. 2 we show the temporal evolution of the internuclear distribution when only a single pulse is used for the excitation. The time-of-flight spectra from which Fig. 2 is derived were obtained by subtracting a reference spectrum, obtained without the probe pulse, from the recorded spectra. Ground-state depletion by the pump pulse is observed. However, in the time-of-flight region where the time-dependent signal lies, the background signal is small, so scaling of the reference signal to take into account the depletion does not significantly change the displayed signal. The measured internuclear distributions are based on recording the kinetic energies of I^+ ions created when the probe pulse ($I \sim 5 \times 10^{13}$ W/cm^2) projects the excited molecules onto the Coulombic I^+-I^+ potential (see Fig. 1). The internuclear distance is extracted from the measured energy [12] by assuming that this energy is the sum of the Coulomb energy and the fragment's kinetic energy prior to ionization (~220 meV). Figure 2 is essentially a series of snapshots, at different times, of iodine molecules dissociating with a speed of 11.6 Å/ps. Since photodissociation of diatomic molecules is well understood, we use it to test the spatial resolution of our method of measurement. The width of the internuclear wave function of the dissociating molecules is determined by the bandwidth, the duration, and the phase relation between the different frequency components (the chirp) of the pump pulse. A classical simulation of the dissociation induced by a chirp-free 625-nm, 80-fs pump pulse shows that the width of the wave function is ~1.3 Å at 400 fs after excitation and ~2.0 Å at 900 fs after excitation [15]. This should be compared with the typical size of 2–3 Å of the measured internuclear structures in Fig. 2. The smooth evolution of the wave function confirms that resonances in the ionization process are not important in this range of internuclear distances.

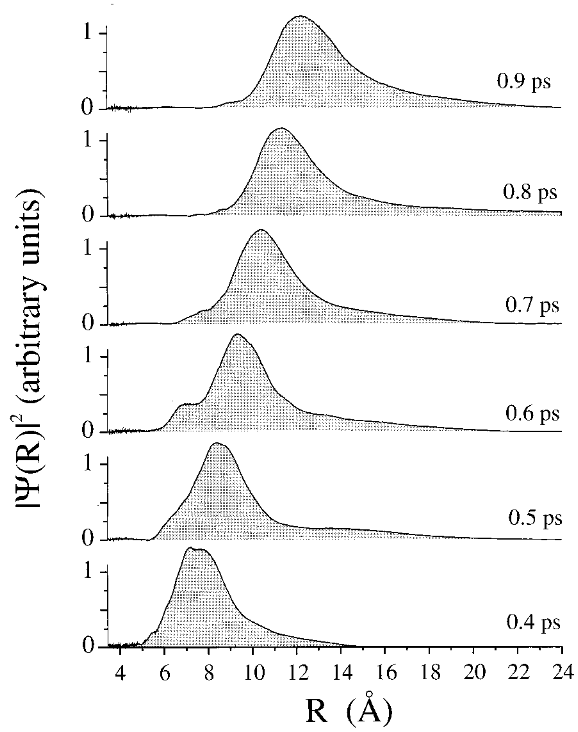

FIG. 2. The square of the internuclear wave function, $|\Psi(R)|^2$, of the dissociating I_2 molecule measured at different times after excitation by a single pump pulse. Each trace is an average of 2000 laser shots.

Our spatial resolution is primarily limited by the energy resolution of the time-of-flight ion spectrometer [15]. In future studies a high-energy-resolution spectrometer should enable us to reach the ultimate spatial resolution limit determined by the effective duration of the probe pulse. The motion of the nuclei during the probe pulse leads to a blur of the measured internuclear position approximately equal to the product of the internuclear velocity and the effective pulse duration. This effective pulse duration is expected to be only a fraction of the real duration, since the multiple ionization only occurs around the peak intensity of the probe pulse. In addition, high power pulses of 10–20 fs duration, already produced [16], will further improve the spatial resolution. Thus, measurements with a resolution of a few tenths of an angstrom seem perfectly feasible even for fast internuclear velocities of 10–40 Å/ps.

The situation where two pump pulses are used is illustrated in Fig. 3. Now we measure the internuclear distribution ~810 fs after the molecules are exposed to the first pump pulse and therefore ~500 fs after exposure to the second pump pulse. The different traces reflect different relative

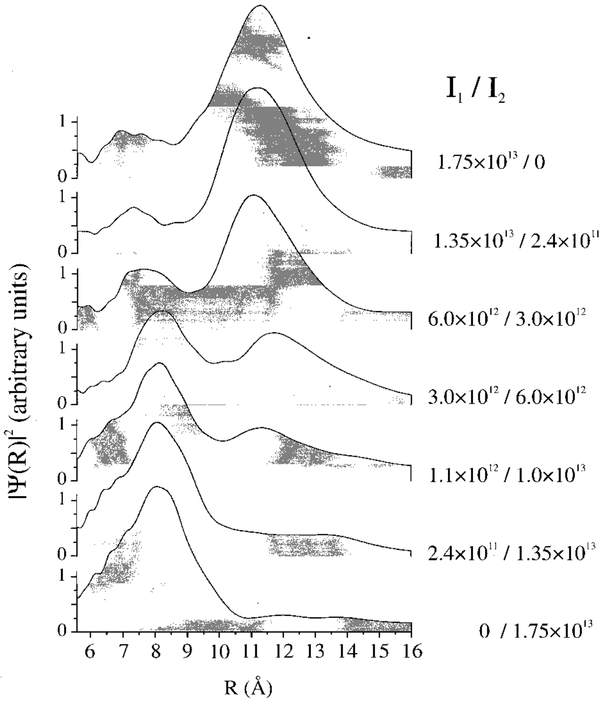

FIG. 3. The square of the internuclear wave function, $|\Psi(R)|^2$, when two pump pulses are used to dissociate iodine. The different traces correspond to different intensity ratios I_1/I_2, of the two pump pulses (units for intensity is W/cm^2). Each trace is an average of 2000 laser shots and is recorded ~810 and 500 fs after exposure to the first and the second pump pulses, respectively.

intensities of the two pump pulses. Figure 3 shows how the shape of the square of the internuclear wave function can be controlled simply by changing the intensity ratio between the first and the second pump pulse. Figure 3 serves a dual purpose of demonstrating the formation and control of quantum picostructures and our ability to measure them by resolving a double-peaked structure separated by ~3.6 Å (310 fs×11.6 Å/ps).

Wave-function measurements require both amplitude and position information. In the upper trace of Fig. 3 a single-peaked structure centered at ~11.5 Å is observed, since only the first pump pulse is used. As the intensity of the first pump pulse is gradually decreased and the intensity of the second pump pulse gradually increased, the amplitude of the 11.5-Å peak decreases and the amplitude of the peak at ~8 Å increases. Eventually, the quantum picostructure consists of a single-peaked wave function located at 8 Å when only the second pump pulse is employed (lower trace). In the middle trace in Fig. 3, approximately 55% of the probability density is localized around 8 Å and ~45% is localized around 11.5 Å (based on peak amplitudes). Since the quantum picostructures are prepared by single-photon excitation (Fig. 1), the transition rate is proportional to the number of photons. One therefore expects that the intensity ratio of the two pump pulses (45%/55%) is reflected in the wave function in the limit of no saturation. However, the middle trace was recorded with an intensity of 3.0×10^{12} W/cm^2 for the first and the second pump pulse, respectively. Thus, it seems likely that the first pulse partially depletes the population of the ground-state I_2 molecules.

There is another effect related to the intensity of the pump pulses that can influence the creation of the quantum picostructures. In order to achieve a high transition rate in the single-photon process used for the formation of the quantum picostructures (Fig. 1) the fluence of the pump pulses must be high. However, this inevitably leads to high intensity of the pump pulses due to their short duration. At the intensities employed in our experiment, the I_2 molecules are therefore likely to be excited not just to the $A\,^3\Pi_u$ state by one-photon absorption but also at higher-lying states by multiphoton absorption [15]. In general, this will lead to dissociation via different potential curves and therefore to creation or a more complex quantum picostructure. As is discussed in more detail elsewhere [15], our data in Fig. 3 are slightly perturbed by a fraction of the I_2 molecules that dissociate after two- or three-photon absorption. For instance, the small peak at ~7-8 Å in the uppermost spectrum of Fig. 3, where the intensity of the second pump pulse is zero, is likely due to such multiphoton excitations induced by the first pump pulse. If desired, higher-order processes can be significantly suppressed by lowering the overall intensity of the pump pulses. Even though the single-photon excitation probability per pump pulse will be reduced when the intensity is lowered, the total excitation probability can still be significant if a sequence of 10–20 pulses is used to form a quantum grating.

It is fundamental to quantum mechanics that the two peaks observed in Fig. 3 correspond to a coherent superposition of two wave packets consisting of internuclear continuum wave functions localized around two internuclear separations. Any molecule within the excitation volume, irrespective of its properties, experiences two sequential pulses (or equivalently, a single pulse that happens to have a double-peaked structure). Quantum mechanics does not allow us to say from which pulse the photon was absorbed. At the early times after their formation, the two peaks are expected to be completely separated, since they are formed by two 80-fs pulses separated by 310 fs. The fact that the observed peaks are not completely separated (see the three middle traces in Fig. 3) is due to the insufficient energy resolution of our ion spectrometer and possibly to nonlinear excitation processes. At longer times after their formation, the two wave packets are expected to overlap since the fast part of the last excited wave packet will catch up with and eventually pass the slowest part of the first excited wave packet. Interference effects between the overlapping internuclear wave packets should be observable in future experiments, since, in our case, the femtosecond pulses used for their formation have a well-defined and fixed phase relation in all the (highly confined) probed volume.

Our measurements point to several different directions in femtosecond molecular dynamics. (1) Multiphoton ionization not only provides a method for probing molecular dynamics, but it can also be used as an efficient means to initiate dynamics. Although it is not yet clear whether multiphoton ionization can be controlled with enough precision to produce ionic quantum picostructures, it will be useful in the production of new excited states that can be studied with femtosecond probe pulses [11]. (2) Quantum picostructures can be produced using femtosecond pulse-shaping techniques [17], permitting the formation of much more elaborate internuclear structures. Each individual pulse in a pulse train can be designed to have the appropriate duration, amplitude, and phase to create a desired quantum picostructure [18]. Thus, it seems feasible to readily construct a grating-like structure along an internuclear axis [7]. This will be a simple test bed for quantum-optics experiments similar to those discussed for spontaneous emission [19]. It may be possible to examine interference phenomena occurring in, e.g., light scattering from, or ionization of, the quantum grating simply by adjusting the temporal separation or the phase relation between the individual pump pulses. (3) Instead of constructing quantum picostructures artificially, as we have done here, they are produced naturally in such photochemical events as predissociation [20]. Temporally resolved Coulomb explosions provide an alternative diagnostic of predissociation of molecules. (4) Pump-probe experiments carried out in the strong-field limit provide a different approach to femtosecond time-resolved measurements. Unrelated to traditional frequency resolved spectroscopy, such experiments hold the promise of a unique insight into fast molecular dynamics of diatomics and polyatomics and of spectroscopic information. As an inherently short-pulse technique, strong-field probing is not restricted by bandwidth or fluence limitations that normally affect perturbative techniques in the short-pulse limit. Finally, intense probe pulses promise time resolution significantly shorter than the pulse duration of the probe laser.

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[1] J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991).

[2] M. Welland, Phys. World **7**, 32 (1994).

[3] C. N. Cohen-Tannoudji and W. D. Phillips, Phys. Today **43** (10), 33 (1990).

[4] M. Sigel and J. Mlynek, Phys. World **6**, 36 (1993).

[5] *Femtosecond Chemistry*, edited by J. Manz and L. Woste (VCH, Weinheim, 1995).

[6] Manipulation of the electronic wave function of atomic Rydberg states has recently been demonstrated: D. W. Schumacher, J. H. Hoogenraad, D. Pinkos, and P. H. Bucksbaum, Phys. Rev. A **52**, 4719 (1995); M. W. Noel and C. R. Stroud, Bull. Am. Phys. Soc. **41**, 1115 (1996).

[7] B. Kohler *et al.*, Acc. Chem. Res. **28**, 133 (1995).

[8] S. Augst, D. D. Meyerhofer, D. Strickland, and S. L. Chin, J. Opt. Soc. Am. B **8**, 858 (1991); M. A. Ammosov, N. B. Delone, and V. P. Krainov, Zh. Eksp. Teor. Fiz. **91**, 2008 (1986) [Sov. Phys. JETP **64**, 1191 (1986)].

[9] T. Seideman, M. Y. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).

[10] S. L. Chin, C. Rolland, P. B. Corkum, and P. Kelly, Phys. Rev. Lett. **61**, 153 (1988).

[11] E. Constant, H. Stapelfeldt, and P. B. Corkum, Phys. Rev. Lett. **76**, 4140 (1996); D. M. Villeneuve, M. Yu. Ivanov, and P. B. Corkum, Phys. Rev. A **54**, 736 (1996).

[12] H. Stapelfeldt, E. Constant, and P. B. Corkum, Phys. Rev. Lett. **74**, 3780 (1995).

[13] P. B. Corkum, M. Yu Ivanov, and J. S. Wright, Annu. Rev. Phys. Chem. (to be published).

[14] We measure the square of the wave function; our method of measurement is not sensitive to the phase of the wave function.

[15] H. Stapelfeldt, E. Constant, H. Sakai, and P. B. Corkum (unpublished).

[16] M. Nisoli, S. De Silvestri, and O. Svelto, Appl. Phys. Lett. **68**, 2793 (1996); S. Backus *et al.*, Opt. Lett. **20**, 2000 (1995).

[17] A. M. Weiner, Prog. Quantum Electron. **19**, 161 (1995); M. M. Wefers and K. A. Nelson, Science **262**, 1381 (1993).

[18] B. Kohler *et al.*, Phys. Rev. Lett. **74**, 3360 (1995).

[19] K. Rzazewski and W. Zakowicz, J. Phys. B **25**, L319 (1992).

[20] A. H. Zewail, Faraday Discuss. Chem. Soc. **91**, 1 (1991); M. J. J. Vrakking, D. M. Villeneuve, and A. Stolow J. Chem. Phys. **105**, 5647 (1996).