References and Notes

12. For crystals composed of Ag and Au nanoparticles, the lattice is isostructural with sphalerite ZnS (216). For crystals made of only one type of metal cores (compare Fig. 5B), the lattice is best described as diamond (SG 227).
13. To account for both of these possibilities we use “diamond-like” nomenclature in the text.
15. Supporting material is available on Science Online.
17. After the evacuation of the “good” solvent, the NP crystals constituted only ~0.01% v/v of the remaining solution, so crystallization cannot be attributed to confinement effects that might have been operative had all liquid been evaporated.
19. This estimate is based on the Deryagin-Landau-Verwey-Overbeek (DLVO) theory and for a 1:1 electrolyte. Specifically, \( z_{\text{eff}} = \frac{z_{\text{eff}}}{2} 
\) where \( \epsilon \), \( \epsilon_{0} \), \( \epsilon_{0} + \epsilon_{\text{eff}} \) are the static dielectric constant of the medium, and \( \epsilon_{\text{eff}} \) is the permittivity of vacuum. Using EDS, we determined the content of Cl to be ~3%, which corresponds to a concentration \( c = 10^{-7} \text{ M} \) of the residual ammonium salt (NMe₄)⁺(Cl⁻) present in the crystal. Assuming that the effective dielectric constant of a mixture of water and DMSO filling the free space between the NPs in the crystal can be approximated as \( \epsilon = \epsilon_{\text{water}} + \epsilon_{\text{DMSO}} \), we emphasize that the number can only be treated as an estimate, because with NPs several nanometers in diameter, we are at the limit of applicability of the DLVO mean-field approach. At the same time, our approximation is qualitatively correct as verified by recent numerical Monte Carlo simulations of pairs of nanometer-sized charged particles (20).
25. Because each NP is covered with a SAM, the only dispersion (van der Waals) interaction that needs to be considered is that between alkyl chains of MUA and TMA thiol that form the SAMs. This attractive interaction is important only if the SAMs interpenetrate; it vanishes at distances larger than ~1 nm, and its characteristic energy (assuming ideal parallel alignment of two alkyl chains)—is on the order of \( k_{B} T / \text{CH}_{2} \text{ group} \leq 27 \). TEM images of the charged NPs that we used reveal that the SAMs are “rigid” (i.e., their thicknesses between aggregated NPs are the same as those on isolated one) and that no interpenetration takes place. This observation is easily rationalized by noting that possible interpenetration of the alkyl chains would have to take place at the expense of favorable electrostatic interactions between oppositely charged head groups. Overall, the van der Waals forces in our system can be neglected even if two NPs touch each other. At such small separations, the interactions are dominated by attractive electrostatic forces. Finally, we note that entropic forces due to SAM squeezing (28) are also negligible, because the SAMs are not “compressible.”
29. Results of recent molecular dynamics simulations (22) indicate that mean-field screening concepts can be extended to the nanoscale and can be used to approximate electrostatic forces acting between nanoparticles screened by counterions comparable in size (within one order of magnitude) and present in small quantities (a few layers). Although quantitative analogies could thus be justified, we restrict our discussion to qualitative arguments that are sufficient to explain experimental observations.
40. We thank J.-G. Zheng and M. Kowki for helpful discussions. B.A.G. gratefully acknowledges financial support from the Camille and Henry Dreyfus New Faculty Awards Program, NSF (grant 0503673), and the American Chemical Society Petroleum Research Fund (Award 42953-AC5). K.J.M.B. was supported by the NSF Graduate Fellowship.

Probing Proton Dynamics in Molecules on an Attosecond Time Scale


We demonstrate a technique that uses high-order harmonic generation in molecules to probe nuclear dynamics and structural rearrangement on a subfemtosecond time scale. The chirped nature of the electron wavepacket produced by laser ionization in a strong field gives rise to a similar chirp in the photons emitted upon electron-ion recombination. Use of this chirp in the emitted light allows information about nuclear dynamics to be gained with 100-attosecond temporal resolution, from excitation by an 8-femtosecond pulse, in a single laser shot. Measurements on molecular hydrogen and deuterium agreed well with calculations of ultrafast nuclear dynamics in the H₂⁺, H₂, and D₂ molecules, confirming the validity of the method. We then measured harmonic spectra from CH₄ and CD₄ to demonstrate a few-femtosecond time scale for the onset of proton rearrangement in methane upon ionization.

There is currently great interest in the development of methods to probe the dynamical behavior of matter on the attosecond (1 as = 10⁻¹⁸ s) time scale (1–3). It is known that the ionization of an atom or molecule by an intense laser field and subsequent electron acceleration in the field results in the formation of a chirped electron wavepacket—a “burst” of electrons with a broad range of kinetic energies that recollide with the parent ion over a range of time delays (4). However, the chirp of the electron wavepacket is a hitherto unexploited property in the measurement of ultrafast dynamical behavior. The technique demonstrated here is based on high harmonic generation (HHG) from molecules. HHG is well understood within the framework of a semiclassical model (5), which separates the process into three distinct steps. In the first step, an intense laser pulse ionizes an atom or molecule, launching an electron wavepacket into the continuum. In the next step, the electron wavepacket moves in response to the laser electric field; it is first accelerated away from the parent ion and then returns at some later time (typically 0.5 to 1.6 fs for a laser field at a wavelength of ~800 nm) as the laser field reverses direction. The third step is the recombination of the electron with the parent ion and the emission of a high-energy photon (~10 to 500 eV) that carries away, at discrete multiples of the laser frequency (6), the kinetic energy gained by the electron in the process. The intensity of the radiation emitted at the moment of recombination depends upon the transition amplitude between the wave function de-
scribing the electron and ion at this instant and the initial molecular ground state. Lein (7) showed theoretically that the harmonic signal in a molecule will be approximately proportional to the squared modulus of the nuclear autocorrelation function, which is the overlap between the initial and final nuclear parts of the molecular wave function that evolves from the moment of ionization until the point of recollision. Details of the nuclear dynamics are therefore encoded in the HHG signal, which is blind to all other competing channels because the quantum mechanical path for the molecule starts and ends in the same state.

Our method (Fig. 1) can be viewed as a pump-probe technique. The ionization step of harmonic emission is the pump, because in the case of a molecule, a nuclear wavepacket is simultaneously launched at the moment of ionization. The probe is the recollision of the electron wavepacket with the parent ion, with the nuclear wavepacket information encoded in the emitted harmonics.

The use of the recollision as a probe is broadly related to earlier experiments by Niikura et al., who used the correlation of electron and nuclear wavepackets (1, 2) to provide information about the instantaneous average internuclear separation with subfemtosecond temporal resolution. In that work, the kinetic energy released in recollision-induced fragmentation was used for the probe signal, and thus the temporal resolution was limited to ~0.5 fs by the inherent temporal spread of the recolliding electron bunch. A further limitation was the requirement to tune the laser wavelength over a wide range to vary the pump-probe delays. The kinetic energy release technique has so far been restricted to observing motion along the internuclear axis of diatomic molecules; it is also affected by competing excitation channels. In contrast, our method measures the quantum mechanical nuclear dynamics by determining the overlap integral between the wave function at two times, so it is sensitive to motion in any direction. Further, by using the chirp associated with harmonic emission (4) to probe the nuclear motion, we attain ~100-as time resolution as well as access to a range of pump-probe time delays for a single laser pulse at fixed wavelength.

The high temporal resolution available in our technique arises from the chirped nature of the recolliding electron wavepacket (Fig. 2). Electrons born into the continuum between ~5/4 to 3/4 of an optical cycle after the laser field maximum and the next zero of the field follow so-called “short trajectories” (8) that return quickly to the core. Each of these short trajectories returns to the parent ion at a different delay time Δt, and each is associated with a different electron kinetic energy at the point of recollision. This temporal spread leads to a frequency-chirped harmonic emission, with successively higher harmonics being generated at longer time delays, as has been directly measured by Mairesse et al. (4). This property of HHG is fundamental to the technique demonstrated here, because it allows a range of pump-probe delays to be accessed by analysis of a single harmonic spectrum. In principle, a second set of longer trajectories can contribute to the HHG spectrum, with the electron born earlier and returning later to the core, but in this experiment these long trajectories are filtered out from the spectrum, yielding a one-to-one mapping between delay and photon frequency (Fig. 2). Simply recording the harmonic spectrum therefore allows us to probe the nuclear motion over a range of pump-probe time delays set by the temporal spread of the recolliding electron wavepacket.

We implement this method by observing the ratio of the harmonic spectra generated in gaseous H2 and D2, or CH4 and CD4. The use of isotopes ensures that the variation in HHG spectra is due primarily to differing nuclear dynamics, because the electronic states are very similar. The variation of this ratio with harmonic order then yields information concerning the differing nuclear (proton or deuteron) dynamics in the ions of the two species, with the 100-as time resolution encoded in the frequency of the emitted radiation over a range of ~1 fs for laser light of ~800 nm wavelength. The HHG efficiency decreases more over a given range of harmonic orders for H2 than for D2 because of faster nuclear motion in the lighter molecule.

![Fig. 1. Pump-probe method for measuring proton dynamics in molecules.](http://science.sciencemag.org/)

**A** The experimental setup required to observe high-harmonic emission. (B) Ionization serves as the pump process because it launches an electron wavepacket into the continuum simultaneously with a nuclear wavepacket on the H2+ ground state potential surface (c). The electron wavepacket then moves in response to the laser field, returning to the parent ion with an increased kinetic energy at some later time. The recollision acts as the probe of the nuclear motion that has occurred in the time delay since ionization occurred.

We used very short laser pulses in this experiment to freeze rotational motion. We generated 8-fs pulses centered at a wavelength of ~775 nm with the use of a gas-filled hollow fiber and chirped mirrors to compress ~0.75-nJ, 30-fs pulses. The laser beam was focused by an off-axis paraboloid mirror (focal length 400 mm) into a pulsed gas jet (Fig. 1A). The focus was located 9 mm before the gas jet to ensure that short electron trajectories dominated the harmonic signal. The intensity at the interaction region was estimated to be 2 × 1014 W cm–2. The harmonic signal was spectrally dispersed in a grazing-incidence, angularly resolving, flat-field spectrometer and was detected by an extreme ultraviolet–sensitive imaging microchannel plate detector, with a charge-coupled device (CCD) camera used for readout. The harmonic spectrum was extracted by angular integration of the CCD images. Because the first ionization potential in the two species is very similar (15.43 eV for H2, 15.46 eV for D2 (9)), differences in phase-matching conditions for harmonic generation in the two cases were negligible: The harmonics generated in H2 and D2 had identical far-field angular distributions.

It was essential that each gas (e.g., H2 or D2) was delivered to the interaction region at an equal...
density. We ensured this condition by using a high-intensity, 800-fs laser field at 1053 nm to fully ionize the gas, and performing interferometric measurements and Abel inversion to characterize the electron density. The experimentally determined backing pressure ratio, $P(D_2)/P(H_2)$, that was found to equalize the electron (and therefore molecular) density was $1.3 \pm 0.1$. This ratio was measured with a species-independent piezoelectric gauge in the gas jet backing line and agrees, within experimental error, with gas flow calculations and other tests based on the pressure jump in the interaction chamber after pulsing the valve a fixed number of times with the vacuum pumps off.

Typical high-harmonic spectra from $H_2$ and $D_2$ at equal density are shown in Fig. 3A. Spectra were averaged over 400 laser shots, although it should be noted that the full dynamical information is encoded in each spectrum recorded. In agreement with Lein’s predictions, Fig. 3A shows that the harmonic signal at all orders detected is higher in $D_2$ than in $H_2$, a clear signature of the slower nuclear motion occurring in $D_2$. As expected from the different speeds of nuclear motion, we see a significant increase in the $D_2/H_2$ HHG intensity ratio as the frequency of the harmonic, and therefore the time delay, increases (Fig. 3B).

We compared our experimental results with a calculation based on the strong-field approximation, which collects the effect of the nuclear motion in the compact nuclear correlation function ($10$). The harmonics are approximately proportional to the squared modulus of the nuclear autocorrelation function, $c(t) = \int \chi(R,0)\chi(R,t)dR$, where $\chi(R,t)$ are the initial and propagated vibrational wavepackets in the molecular ion, $R$ is the internuclear distance, and $t$ is the electron travel time (equivalent to our delay time, $\Delta t$). For geometrical reasons, most of the molecules in the randomly aligned sample in our experiment have their molecular axes nearly perpendicular to the laser electric field direction, which reduces the effect of two-center interference ($11$) and minimizes Stark shifts ($12$). We have confirmed in test calculations that the influence of the Stark shifts in the Born-Oppenheimer potential is negligible for the present set of parameters. Two-center interference gives rise to a small but clearly discernable shift and has been included in our analysis. For random orientation, this effect can be taken into account by using the nuclear correlation function $c(t,k) = \int \chi(R,0)\chi(R,t)/|k|RdR$ including the interference kernel $s(k,R) = \sin(kR)/(kR/2)$. Here, $k$ is the wave vector of the recolliding electron, evaluated using the relation $\hbar^2k^2/(2m) = \hbar\omega$ ($13$), where $\hbar$ is Planck’s constant divided by $2\pi$, and $\hbar\omega$ is the energy of the harmonic being emitted upon recombination. The ratio of harmonic intensities $D_2/H_2$ is calculated by taking the ratio of the squared modulus of the two correlation functions for $D_2$ and $H_2$. The calculated curve is scaled to account for the slight difference in photoionization cross sections for $H_2$ and $D_2$ ($14$). We found good quantitative agreement between our measurements and the calculation (Fig. 3B).

The nuclear wave function $\chi(R,t)$ and, from this, the time evolution of the expectation value of $R$ ($\langle R(t) \rangle$) in each molecule was reconstructed from the recorded intensity spectra and their ratio by use of a genetic algorithm ($7$, $10$). Agreement with the exact calculation is good (Fig. 3C). Therefore, the measurement of the harmonic spectrum ratio can be used to determine proton (deuterium) motion in $H_2$ and $D_2$ molecules. $\sim 1$ ps after ionization, with a temporal resolution of $\sim 100$ fs (the difference in recollision times between successive harmonic orders). Here we use the data from $H_2/D_2$ primarily to test and confirm the method, as the potential surface and thus the calculated dynamics of the proton are known in the case of $H_2$. Therefore, agreement between the measurement and the calculated ratio of the nuclear correlation function (Fig. 3B) is confirmation that the chirp of the electron is satisfactorily given by the semiclassical treatment, validating the frequency-time mapping. With this confirmation, we can apply the technique to other molecules for which the potentials are not fully known.

The HHG spectrum is determined by the squared modulus of $c(t)$ and of the remaining parts $d(\omega)$ of the transition dipole moment that do not depend on the nuclear motion. Similar to Itatani et al. ($13$), we write $d(\omega) = a(\omega)[k(\omega)]l(\omega)$, where $a(\omega)$ is the amplitude for an electron of wave vector $k$, and $l(\omega)$ is the recombination part of $d(\omega)$. It is feasible to directly calibrate the factor $d(\omega)$ by measuring a given harmonic over a range of laser intensities (so that $l(\omega)$ would be fixed but the recollision time would be changing with laser intensity). An auxiliary measurement on an atom of similar ionization potential would be used to establish the variation of $a(\omega)$ with recollision time. In our implementation of the method, the equivalence of $a(\omega)$ for the protonated and deuterated species has been used to remove the spectral variation of this factor. This simplification is experimentally convenient, as then the main technical difficulty is simply to ensure equal particle densities in the comparison, with only a single set of measurements being required at a fixed and known laser intensity.

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**Fig. 2.** Encoding of nuclear dynamics within harmonic spectra. Upper panel: The trajectory of the ionized electron differs depending on the exact time of ionization. Three possible electron trajectories labeled 1, 2, and 3 are shown, which recollide with the molecular ion after delays $\Delta t_1$, $\Delta t_2$, and $\Delta t_3$ with increasing kinetic energy $E_1$, $E_2$, and $E_3$, resulting in the emission of increasingly higher frequencies photons after recombination (shown as the 17th, 25th, and 33rd harmonics for the purpose of this illustration). Note: Although the curves in the lower panel are physically accurate, the electron trajectories shown in the upper panel have been slightly altered to improve clarity.
To further explore the application of this technique, we compared harmonic spectra obtained in CH4 and CD4 (Fig. 4A). We observed behavior consistent with our studies of D2 and H2. The harmonic yield is found to be greater in the hexagonal isotope whose nuclei are expected to move more slowly, and this effect is found to be enhanced for the higher order harmonics, which probe the parent molecule at a longer time delay. The differing photoabsorption cross sections in CH4 and CD4 (16), although making a small contribution to the measured ratio, cannot account for the increase in the ratio that we observe. These results therefore confirm that this technique is not limited to probing nuclear wavepackets in diatomic molecules.

It is known from theory (17) and experiment (18, 19) that although the CH4 molecule has the well-known tetrahedral structure (with 109.5° bond angles), CH4+ adopts a C2v geometry, with some bond angles diminishing to <60° (Fig. 4B). It is anticipated that these structural rearrangements at the moment of ionization must be fast, as the tetrahedral structure of methane is far from the equilibrium bond angles of the ion. Our measurements provide direct evidence that the time scale for the onset of this structural rearrangement is on the order of a few femtoseconds. The measured ratio (Fig. 4A) is the square of the ratio of the molecular autocorrelation functions for the two species, a quantity that can be calculated directly from the molecular potentials. Therefore, the measurement can be used to test the correctness of computed potentials.

Several extensions of the technique are possible. Use of a driving laser field of a longer wavelength would extend the time window over which information on the nuclear dynamics can be gained, for instance, a field at a wavelength of 2 μm would allow motion to be followed for up to 4 fs after ionization. This could also be achieved by selection of the long-trajectory component of the chirped electron wavepacket for harmonic emission without affecting the temporal resolution of the measurement. A further extension of the technique may be to study neutral molecular dynamics by starting from negative molecular ions formed through electron attachment.

Our technique is sensitive to the initial few femtoseconds after the electronic change (e.g., photoionization) that drives the motion of the protons toward a new equilibrium position. In contrast, conventional methods only provide data for the potential energy surface around the equilibrium position and do not access the extremely fast proton rearrangement that follows directly from electronic changes. Our technique may therefore provide new insights into some of the most fundamental events in chemistry.

References and Notes
10. See supporting material on Science Online.
20. We thank J. Lazarus and M. Hohenberger for assistance with the interferometric measurements of the gas densities; L. Chipperfield, P. L. Knight, R. Torres, and C. Latimer for valuable scientific discussions; and P. Routhen, A. Gregory, and B. Ratnaekeara for technical assistance. Supported by the Research Councils UK through the Basic Technology Programme and the Engineering and Physical Sciences Research Council.

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