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Observation of fractional revivals of a molecular wave packet

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The study and control of molecular dynamics through the use of femtosecond laser techniques require an understanding of various orders of molecular wave-packet phenomena such as revivals. We present the observation of fractional revivals in a vibrational wave packet: the B state of the Br_2 molecule. Fractional revivals occur in anharmonic systems at characteristic times in the nonclassical regime when, due to dephasing between vibrational eigenstates, the wave packet partially localizes into sub-wave-packets. Half and quarter revivals were clearly observed, as well as indications of one-sixth revivals. [S1050-2947(96)50707-9]

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There is considerable interest in investigating molecular dynamics through the use of coherent superposition states. Molecular wave packets have provided examples of classical-like motion on bound, unbound, and nonadiabatically coupled potential-energy surfaces [1–5]. Atomic Rydberg wave packets have been illustrative of the ability of quantized systems to take on characteristics, such as spatial localization, that one is accustomed to in classical sytems [6–16]. In general, quantum systems exhibit a decay of the classical-like behavior due to dephasing between eigenstates. For some quantum systems, the classical-like behavior can recur at longer times and this is known as a revival [7]. In the period between the initial decay and the revival, these systems behave nonclassically. However, at specific times in the nonclassical region, interesting partial localizations of the wave packet can occur and these are known as fractional revivals [17]. In this Rapid Communication, we present their observation in a molecular system.

The current effort to control molecular dynamics through the use of wave packets prepared by shaped femtosecond pulses [18–20] demands a detailed understanding of the various orders of molecular wave-packet phenomena and, therefore, a recognition of differences between atomic and molecular behavior. In an atomic system, there is only one ‘‘detection point’’ for the wave-packet motion—at the atomic core. Therefore, the direct observation of harmonics of the wave-packet motion is indicative of wave-packet phenomena such as fractional revivals. This is not the case in molecular systems because the ‘‘detection point’’ is determined by Franck-Condon factors that depend on the details of the potential-energy surfaces involved. For example, in diatomic molecules, if the Condon point (the stationary phase point of the Franck-Condon integral) is not at a turning point [5], the wave packet is detected twice per period, leading to the observation of harmonics. The same will be true for the existence of more than one Condon point—a phenomenon for which there is no atomic analogue. Furthermore, nonadiabatic curve coupling effects (quite common in molecular excited states) present complex wave-packet evolution, which can lead to observations that appear somewhat reminiscent of fractional revivals. A clear example of this is provided by the well-known NaI system [2,21]. Therefore, as distinct from atomic systems, the determination of the details of wave-packet motion in molecular systems, such as fractional revivals, requires both knowledge of the relevant potential-energy surfaces and an analysis of the phases of the harmonics of the wave-packet motion.

Consider a bound excited electronic state of a diatomic molecule that is populated by means of a femtosecond laser, creating a vibrational wave packet, $\psi(x,t) = \Sigma_n a_n |n\rangle \exp(-iE_n t/\hbar)$, where $|n\rangle$ is the set of vibrational eigenstates with energies E_n, and the a_n are constant coefficients. A second femtosecond laser probes the wave packet through excitation to a higher electronic state—in our case, the ionic ground state. The ion signal $S(t)$ is detected as a function of the time delay between the two pulses. Within the Franck-Condon picture, the ionization process favors detection of the wave packet near a particular internuclear separation R (the Condon point), and so the signal is expected to come and go periodically as the wave packet travels through this detection window.

The period of the signal is related to the classical frequency of the molecular vibration, ω_c. For example, if the Condon point is at a turning point, one would expect the signal to oscillate at frequency ω_c. The signal is $S(t) = |P(t)|^2$, where $P(t) = \langle f | \vec{\mu} \cdot \vec{E} | \psi(x,t) \rangle = \Sigma_n b_n \exp(-iE_n t/\hbar)$. Here $\langle f|$ represents the final ionic state, $\vec{\mu}$ the transition dipole, $\vec{E}$ the electric field vector of the probe laser, and $b_n = a_n \langle f | \vec{\mu} \cdot \vec{E} | n \rangle$. Therefore

$$S(t) = \sum_{n,m} b_n b_m \cos[(E_n - E_m)t/\hbar]. \tag{1}$$

The signal is composed of beat frequencies between all pairs of energy levels that make up the wave packet. The lowest frequencies correspond to beats between adjacent vibrational levels, $n = m \pm 1$, with a frequency of approximately ω_c. There are also higher frequencies corresponding to beats between further-separated energy levels. In general, frequencies of approximately $\ell \omega_c$ are due to beats between energy levels n and $n - \ell$, where ℓ is an integer.

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Averbukh and Perel'man [17,22] theoretically studied fractional revivals in various systems, and Vetchinkin and co-workers [23,24] have specifically studied revivals in Morse-like anharmonic systems. The energy levels of an anharmonic oscillator can be written as $E_n = \hbar\omega(n - \alpha n^2)$, where ω is the fundamental frequency and α is the anharmonicity parameter. The revival time, $T_{rev} = 2\pi/\omega\alpha$, is the time at which the wave packet is fully reconstituted with its original phases. Averbukh and Perel'man showed that at times $t/T_{rev} = p/q$, where p/q is an irreducible fraction of integers, the phase differences between subsets of the component eigenfunctions are stationary, and the wave packet breaks up into sets of sub-wave-packets. Although there are well-known higher-order corrections to the Morse function, the latter appears to be sufficient to locate the revivals.

In the terminology of Averbukh and Perel'man [17], the first reconstruction of the wave packet [7] is in fact a half-revival, $p/q = \frac{1}{2}$. At this time $T_{rev}/2$, the phase differences of all eigenfunctions are stationary, but the even eigenfunctions $|2n\rangle$ are out of phase by π with the odd eigenfunctions $|2n+1\rangle$. Thus the wavepacket is fully reconstituted but phase shifted by π from the original. Halfway between $t = 0$ and the half revival, at the quarter revival $t = T_{rev}/4$, the wavepacket splits into two sub-wave-packets. Since there are then two wave-packets, each moving with the classical period, the detected signal can have twice the classical frequency.

We can generalize the analysis in order to determine which harmonics are expected for each fractional revival order. From Eq. (1), the phase of the beats between vibrational states $|n\rangle$ and $|m\rangle$ is $\phi_{nm}(t) = (E_n - E_m)t/\hbar = 2\pi(\alpha^{-1} - n - m)(n-m)t/T_{rev}$. The ℓth harmonic of ω_c comes from beats between states $|n\rangle$ and $|n-\ell\rangle$. The phase difference between $|n\rangle$ and $|n-\ell\rangle$ is $\phi_{n,n-\ell}(t) = 2\pi\ell(\alpha^{-1} - 2n + \ell)t/T_{rev}$. We want to find at which times t the phase differences are independent of n modulo 2π, so that all states separated by ℓ can add constructively. This requires that $2n\ell t/T_{rev}$ be an integer, which has solutions $t/T_{rev} = k/(2\ell)$, where k is an integer. Therefore, the lowest-frequency beats ($\ell = 1$) will occur at $t = T_{rev}/2, T_{rev}, \ldots$, while second harmonic beats ($\ell = 2$) will be in phase at $t = T_{rev}/4, T_{rev}/2, 3T_{rev}/4, \ldots$.

The experimental setup is explained in more detail elsewhere [5]. Briefly, a seeded mixture of 1% Br_2 in helium buffer gas was expanded through a skimmed supersonic pulsed valve into a time-of-flight mass spectrometer. Near-infrared, 80-fs Ti:sapphire-laser pulses were amplified in a series of dye cells pumped by a synchronized picosecond Nd:YAG (neodymium-doped yttrium aluminum garnet) laser, split and independently focused into two quartz plates to produce threshold white light continua. Portions of the continuum spectra were reamplified in two further dye amplifier chains, in which the desired wavelengths were selected by interference filters. The output of one of the amplifier chains, at 560 nm, served as the pump pulse that prepared the B-state wave packet. The other amplifier chain operated at 580 nm and was frequency doubled to 290 nm to serve as the probe pulse that projected the wave packet onto the ionic state via two-photon ionization. The formed Br_2^+ ion was detected in the mass spectrometer. The 560- and 290-nm pulses were combined collinearly by means of a dichroic beam splitter and were focused close to the molecular beam. Intensities were less than 10^{10} W/cm^2 for the pump and less than 10^{12} W/cm^2 for the probe, each with recompressed pulse durations of less than 100 fs.

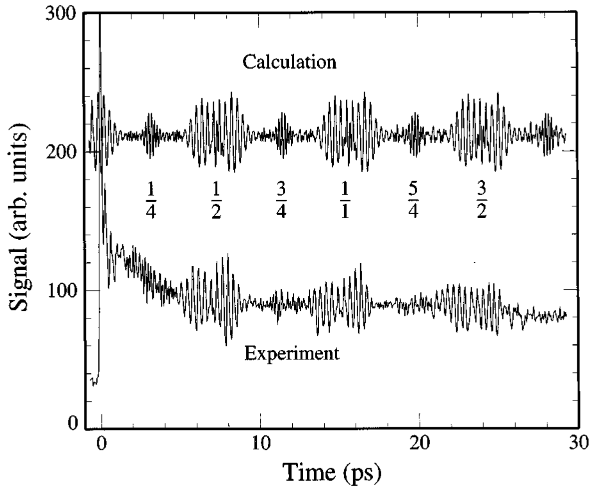

FIG. 1. Pump-probe scan showing Br_2^+ as a function of time delay, with a pump wavelength of 560 nm and a probe wavelength of 290 nm. Bottom trace is experimentally measured, upper trace is calculated. The signal is a measure of when the wave packet is near its inner turning point. Higher-frequency components are due to fractional revivals of the wave packet, as indicated by the assignment ($p/q = \frac{1}{4}, \frac{1}{2}, \ldots$).

The $Br_2{}^+$ signal shown in Fig. 1 was collected as a function of time delay between the pump and probe lasers, and averaged for 100 shots per time delay point. A theoretical simulation based on the exact Rydberg-Klein-Rees (RKR) potential [25] is also shown. Initially, several peaks separated by the classical period of 300 fs are seen. After a few oscillations these peaks disappear due to dephasing of the wave packet. The classical period is not seen again until after 6–9 ps. This is the half-revival of the wave packet, which has been observed previously in diatomic molecules [3,4]. This pattern of dephasing and rephasing is seen to repeat every 8 ps. Based on this, we determine that $T_{rev} = 16$ ps, as expected from the value of $2\pi/\omega\alpha$ derived from a Morse approximation to the B-state potential [25]. What is new here is that higher-order revivals are seen in the nonclassical region at $t = T_{rev}/4, 3T_{rev}/4, \ldots$, where the signal oscillates at twice the classical frequency. These times correspond to the wave packet splitting into two equal parts, out of phase with each other by half the vibrational period.

Figure 2 shows Fourier transform (FT) power spectra of the time delay scan and of the theoretical spectrum from Fig. 1. The individual frequencies correspond to vibrational level spacings $E_n - E_m$ in the B state of Br_2, and are assigned to calculated energy level spacings obtained from exact RKR potentials [25]. The FT contains frequencies around ω_c, $2\omega_c$, and $3\omega_c$. The standard error between the calculated FT based on the RKR data and our observations is 0.1 cm^{-1}. As discussed above, in an atomic system the observation of $2\omega_c$ is indicative of a fractional revival, since there is only one point along the Rydberg trajectory (near the ionic core) where ionization can take place. The observation of harmonics is not sufficient proof of fractional revivals in a

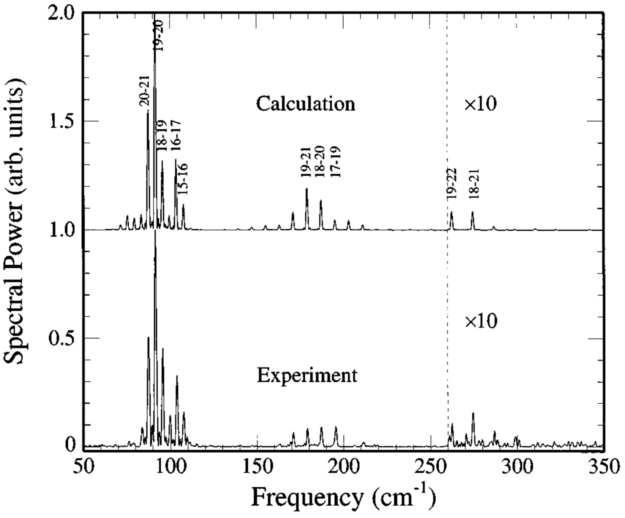

FIG. 2. Fourier transform power spectra of the experimental and calculated data in Fig. 1. The strongest peaks are due to nearest-neighbor coherences. Harmonics are from higher-order coherences. All lines are assigned to level spacings in the Br_2 B state. Data to the right of 260 cm^{-1} have been multiplied by 10. The calculations are based on the exact RKR potential and the standard error between experimental and calculated level spacings is ~ 0.1 cm^{-1}.

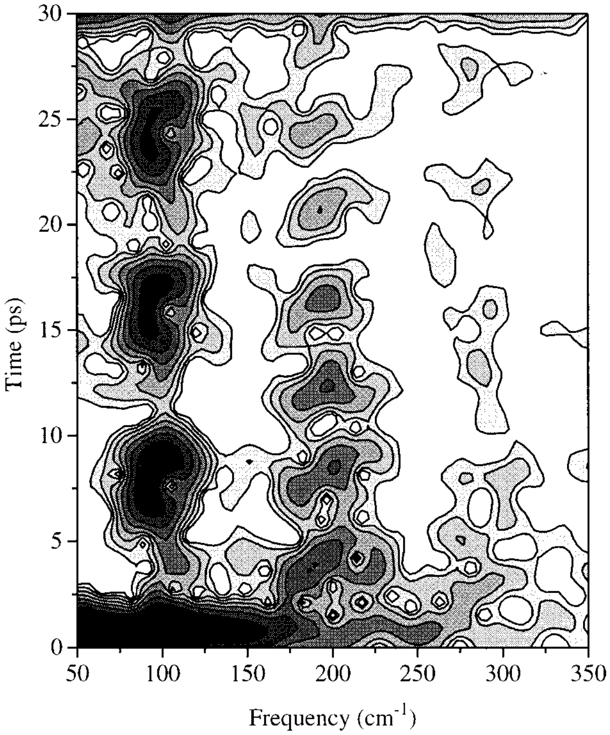

FIG. 3. A spectrogram of the experimental data from Fig. 1 reveals frequency components as a function of time. Half and full revivals of the wave packet are indicated by the presence of the fundamental frequency near 95 cm^{-1}. Quarter revivals are shown by the second harmonic near 190 cm^{-1}. The presence of second harmonic intensity concomitant with the absence of fundamental intensity is proof of a quarter revival. Evidence for the one-sixth revival is seen near 275 cm^{-1}.

molecular system. As discussed above, in addition to fractional revivals, $2\omega_c$ can also be produced by (1) the Condon point not being at the turning point [5], (2) effects due to predissociation on coupled potential-energy curves, or (3) the existence of multiple Condon points. As the B state of Br_2 is known to be well described by a simple potential, the latter two mechanisms do not apply in this case. In order to distinguish between second harmonic frequencies due to the location of the Condon point and those from higher-order fractional revivals, we need to consider the time dependence of the harmonics.

We introduce a spectrogram, which is a sliding-window Fourier transform: $S(\omega,\tau)=\int_0^\infty S(t)g(t-\tau)\exp(-i\omega t)dt$ where $g(t)=\exp(-t^2/t_0^2)$ is the window function. In the following we choose $t_0=1$ ps. This technique has the advantage of portraying frequency and time information simultaneously, at the expense of frequency resolution. In Fig. 3 we show $\ln|S(\omega,\tau)|^2$ as a contour plot. The strongest peaks are near $\omega_c \approx 95$ cm^{-1} and appear every 8 ps. At these times $t/T_{rev}=k/2$, the wave packet resembles a classical oscillator. The second harmonic, $2\omega_c \approx 190$ cm^{-1}, appears every 4 ps. At times $t/T_{rev}=k/4$, the wave packet is split into two equal parts for odd k, and the detection of these two wave packets at the Condon point leads to a signal at $2\omega_c$ and an absence of ω_c. This is clear evidence of a higher-order fractional revival in a vibrational wave packet. (The spectrogram clearly reveals the second harmonic beat that occurs simultaneously with the fundamental: this is difficult to observe in the data of Fig. 1.) There is also evidence of a third harmonic component, $3\omega_c \approx 280$ cm^{-1}, corresponding to revivals of order $k/6$, but this is close to the time-resolution limit imposed by the laser pulses.

To illustrate the relationship between fractional revivals and frequencies in the time delay scans such as in Fig. 1, we have calculated the time delay scan using a simple model. A wave packet was created on the B state by a pump pulse and was allowed to propagate in time, until a second laser pulse ionized it. Rotations and effects due to the turn-on and turn-off of the pulses were not taken into account. The RKR potential-energy function data, from [25,26], were used in the simulations. The calculated scan is compared with the experimental scan in Fig. 1, and the spectrogram of the simulated scan is shown in Fig. 4. The agreement is good.

Figure 5 shows the simulated wave packet $|\psi(x,t)|^2$ at four times, to illustrate the revivals. The original wave packet begins at the inner turning point in (a) and oscillates classically in the potential well with frequency ω_c. After a time the wave packet has completely dephased, (b). In (c) a quarter revival is taking place, whereby the wave packet is composed of two equal parts out of phase, each oscillating with frequency ω_c and giving rise to a signal at $2\omega_c$. In (d) we show the wave packet at the outer turning point during the first half revival; it is once again oscillating classically through the inner turning point with frequency ω_c.

In conclusion, we have made an observation of fractional revivals in a molecular system. The wave packet was seen to periodically dephase and rephase every 8 ps. In the nonclassical region, partial revivals were seen where the wave packet splits into several sub-wave-packets, leading to the observation of harmonics of the classical vibrational frequency. Unlike in atomic systems, knowledge of the relevant potential-energy surfaces and an analysis of the phases of the

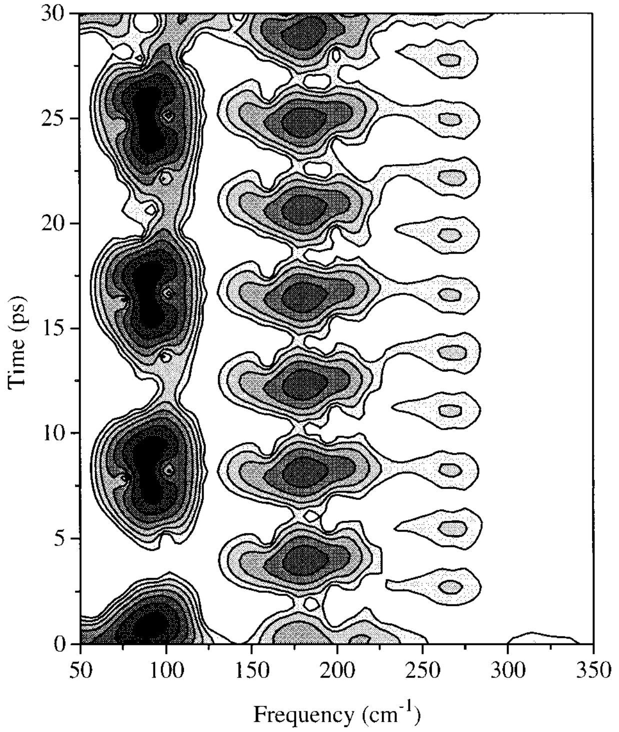

FIG. 4. A spectrogram of the calculated time delay scan from Fig. 1. The ℓth harmonic is an indication of fractional revivals of order $k/(2\ell)$; hence the peaks near 180 cm^{-1} indicate quarter revivals, and peaks near 270 cm^{-1} indicate $\frac{1}{6}$ revivals. The agreement with the experiment (Fig. 3) is good.

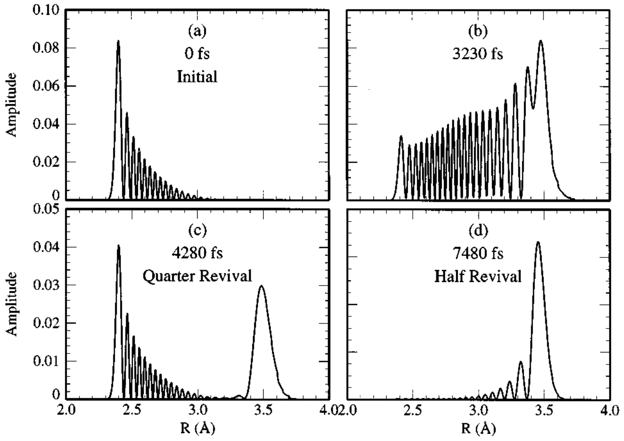

FIG. 5. Four snapshots of the wave packet showing classical and nonclassical behavior. The original wave packet, created by the pump laser at the inner turning point, is shown in (a). This wave packet quickly dephases, leading to a delocalized wave packet in (b). Partial coherences occur at different times, such as at the quarter revival in (c), where the wave packet has split into two sub-wave-packets. In (d), at the half revival, the wave packet has rephased and now looks like the original, except shown at the outer turning point. The quarter revival in (c) can be seen to be the sum of (a) and (d) and corresponds to the doubled frequency seen in Fig. 1 at $p/q = \frac{1}{4}$.

harmonics of wave packet motion are required to differentiate molecular fractional revivals from other molecular wave-packet phenomena. The experimental observations were shown to be in good agreement with a simple model. A detailed knowledge of higher-order wave-packet phenomena will be helpful in the design of femtosecond control experiments for molecular systems.

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[1] *Femtosecond Chemistry*, edited by J. Manz and L. Woste (VCH, Weinheim, 1995).
[2] A. Zewail, *Femtochemistry: Ultrafast Dynamics of the Chemical Bond* (World Scientific, Singapore, 1994).
[3] M. Gruebele and A. H. Zewail, J. Chem. Phys. **98**, 883 (1993).
[4] T. Baumert *et al.*, Chem. Phys. Lett. **191**, 639 (1992).
[5] I. Fischer *et al.*, J. Chem. Phys. **102**, 5566 (1995).
[6] A. ten Wolde *et al.*, Phys. Rev. Lett. **61**, 2099 (1988).
[7] J. A. Yeazell *et al.*, Phys. Rev. Lett. **64**, 2007 (1990).
[8] J. A. Yeazell and C. R. Stroud, Jr., Phys. Rev. A **43**, 5153 (1991).
[9] D. R. Meacher *et al.*, J. Phys. B **24**, L63 (1991).
[10] J. A. Yeazell *et al.*, Phys. Rev. Lett. **70**, 2884 (1993).
[11] J. G. Story *et al.*, Phys. Rev. Lett. **71**, 3431 (1993).
[12] Z. D. Gaeta *et al.*, Phys. Rev. Lett. **73**, 636 (1994).
[13] L. D. Noordam *et al.*, in *Laser Interactions with Atoms, Solids and Plasmas*, edited by R. M. More (Plenum, New York, 1994), p. 163.
[14] M. W. Noel and C. R. Stroud, Jr., Phys. Rev. Lett. **75**, 1252 (1995).
[15] J. Wals *et al.*, Phys. Rev. Lett. **72**, 3783 (1994).
[16] G. Alber and P. Zoller, Phys. Rep. **199**, 231 (1991).
[17] I. Sh. Averbukh and N. F. Perel'man, Sov. Phys. Usp. **34**, 572 (1991).
[18] J. J. Gerdy *et al.*, Chem. Phys. Lett. **171**, 554 (1990).
[19] B. Kohler *et al.*, Phys. Rev. Lett. **74**, 3360 (1995).
[20] C. J. Bardeen *et al.*, Phys. Rev. Lett. **75**, 3410 (1995).
[21] Ch. Meier *et al.*, J. Chem. Phys. **95**, 7337 (1991).
[22] I. Sh. Averbukh and N. F. Perel'man, Phys. Lett. A **139**, 449 (1989).
[23] S. I. Vetchinkin *et al.*, Chem. Phys. Lett. **215**, 11 (1993).
[24] S. I. Vetchinkin and V. V. Eryomin, Chem. Phys. Lett. **222**, 394 (1994).
[25] R. F. Barrow *et al.*, J.Mol. Spectrosc. **51**, 428 (1974).
[26] A. J. Yencha *et al.*, J. Chem. Phys. **99**, 7231 (1995).