Experimental Determination of the Dynamics of a Molecular Nuclear Wave Packet via the Spectra of Spontaneous Emission

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The dynamics of a wave packet in the nuclear degree of freedom of a sodium dimer have been studied via the time- and frequency-resolved spectrum of spontaneous emission. This technique allows one to track the nuclear wave packet dynamics in a single excited electronic state over a substantial fraction of its periodic trajectory. The quantum beats in the spectrum may be partially interpreted in terms of the classical-like evolution of an initially random distribution of internuclear separations. We observe the expansion and contraction of the wave packet that is characteristic of a quadrature squeezed state.

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The excitation of wave packet states of atoms and molecules touches on the boundary between classical mechanics and quantum theory and has been the subject of extensive recent investigations [1]. The wave packet states may be considered classical-like insofar as the probability distribution for the particle's position is well localized—approximating the ideal of a point particle. Spatial localization, the key feature of wave packet states, is achieved by exciting a coherent superposition of many states with large quantum numbers. The large number of eigenstates allows the selection of a single "lobe" of an eigenfunction by quantum interference whereas the high-quantum number requirement forces the selected lobe to have a small spatial extent. Wave packets adhere to the correspondence principle which states that classical behavior is achieved at the limit of large quantum numbers, but with the added stipulation that they contain a large number of eigenstates with a range of quantum numbers.

Wave packet states generally exhibit the special property that certain expectation values can undergo dynamical evolution much like that of a classical point particle traveling along a well-defined trajectory. In an anharmonic potential the wave packet eventually disperses so that it is no longer well localized; however, this process may reverse itself leading to a "revival" of the wave packet. This revival is a result of the discrete spacing of energy levels and is one manifestation of the nonclassical nature of the wave packet [2]. Such behavior has been observed in certain degrees of freedom of atomic electrons [3], molecular nuclear vibrations [4–6], and rotations [7].

Other nonclassical signatures also point out the differences between the wave packet states and classical trajectories, even in the "classical" regimes. One such signature is the spatial extent of the wave packet. It has been predicted, for example, that vibrational quadrature squeezed states can be produced in a harmonic potential if the exciting pulse is a Gaussian whose duration is a non-negligible fraction of the particle's orbital period [8]. It is also possible to generate these squeezed states if the nuclear potential itself is anharmonic, or if there is a change of the nuclear vibrational frequency between the ground and excited electronic states [9]. A characteristic feature of such states is that their position dispersion (a measure of their spatial extent) undergoes periodic evolution at twice the vibrational frequency—the wave packet "breathes," so that at some parts of its periodic trajectory it is quite diffuse. In the case of an anharmonic potential both the "breathing" of the wave packet's spatial extent and the collapses and revivals of the nonclassical regime are a consequence of the same underlying potential.

In order to observe the breathing of the wave packet it is clear that detection of the particle at a single spatial location is insufficient. It is the change in the shape of the wave packet at several different times that must be measured. This can be done by observing the dynamical evolution of the spontaneous emission from the excited electronic state. In contrast to probing the absorption changes induced by the wave packet, detection of the fluorescence allows the selection of the wave packet dynamics in only the excited electronic state of the system.

It is well known that quantum mechanical superposition states exhibit evidence of their mutual coherence in quantum beats in the total or spectrally resolved fluorescence [10], but a classical picture may be usefully developed to describe certain properties of the emission from a molecular wave packet. Consider a wave packet that is generated by a coherent superposition of vibrational levels in a diatomic molecule. The nuclei are initially in their lowest energy state, and the molecule is in its electronic ground state. A short optical pulse that is resonant with the lowest electronic level places the nuclei in a new potential. The transition occurs on a time scale which is short compared to the vibrational period of the nuclear motion. Since the excited state potential surface has a different equilibrium nuclear separation, the nuclei are

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displaced in the new potential and begin to oscillate. At any time the molecule may emit a photon and return to its ground electronic state. The wavelength of the emitted photon will depend on the internuclear separation at the time of emission. More precisely, the fluorescence wavelength depends on the details of the nuclear potential surfaces through the Franck-Condon factors. The time-dependent mean wavelength of the emitted light will oscillate as the nuclei vibrate.

From a quantum mechanical viewpoint the wave packet represents a highly localized nuclear state, from which the transition probability to any other state depends, according to the Franck-Condon principle, on the spatial overlap between the wave packet state and the final state. The overlap between the wave packet and a particular nuclear eigenstate in the electronic ground state will be a maximum as the packet traverses the internuclear separation for which the ground state wave function has a large amplitude. This will occur at separations near the turning points of classical trajectories in the ground state with the same vibrational energy as this wave function. Therefore by both time and frequency resolving the spontaneously emitted radiation it is possible to map out the trajectory of the wave packet. For known vibrational eigenfunctions of the ground and first excited electronic states, it is possible not only to determine the trajectory, but also the shape of the wave packet, at any time, from the shape of the spectrum. It is this feature that exhibits a similar modulation in its width to that of the wave packet's position dispersion [11].

The notion of a time-dependent spectrum of emission may be placed on a rigorous foundation [12]. The electric field radiated by the sample is passed through a time gate that samples it for a specified duration at a fixed delay after an optical pulse excites the sample. The gated fluorescence is then filtered by a spectrometer that restricts the range of observed frequencies around some mean wavelength. This is detected by a square-law detector that measures the total energy passed through both the time gate and frequency filter. By varying the gate delay and the central wavelength of the spectrometer, the time-dependent spectrum of spontaneous emission may be constructed. Its shape is closely related to the shape of the wave packet [12].

In this paper we report the observation of the periodic evolution of the spatial extent of a molecular nuclear wave packet within a single vibrational period. The packet is generated by the coherent excitation of a number of nuclear vibrational states in a Franck-Condon transition by a short optical pulse. The period of oscillation is the same as that of a classical particle of the same mean vibrational energy. The exact character of the wave packet may be calculated by solving Schrödinger's equation for the state amplitudes with the Rabi frequencies calculated in the Born-Oppenheimer approximation, and assuming that the electronic dipole moment is independent of the

internuclear separation. The results of such a calculation are shown in Fig. 1 for a pulse of 60 fs duration exciting vibrational states with mean vibrational quantum number $n = 12$ in the $A\,^1\Sigma_u^+$ state of a sodium dimer at a temperature of 450°C. For temperatures of this magnitude, the thermal distribution in the ground electronic state is significant and is accounted for in this calculation.

The expectation value of the internuclear separation follows exactly the trajectory expected for a classical particle in an anharmonic potential, covering a large portion of its trajectory near the inner turning point very quickly, and the region near the outer turning point quite slowly. During the half-period centered at the outer turning point the wave packet traverses 0.77 Å, whereas for the other half of its cycle, it moves more rapidly covering 0.88 Å.

The position dispersion is modulated at twice the vibrational frequency, so that at the classical turning points the particle is localized to within 0.15 Å or 0.43 times the variance of the thermal distribution for this potential, and as the packet passes the minimum of the potential, the width is 0.42 Å or 1.2 times the thermal variance. The packet undergoes coherent diffusion and relocalization during each vibrational period because the potential in which it moves is anharmonic and because it is generated by a pulse that is approximately 30% of the duration of the vibrational period so that the Vinogradov-Janszky squeezing condition is satisfied [8]. This breathing persists until the wave packet enters the "collapse" regime in which the anharmonicity of the potential causes it to become spatially diffuse during its entire period.

In our experiments, the nuclear vibrational wave packet is formed in a sodium dimer by a one-photon excitation
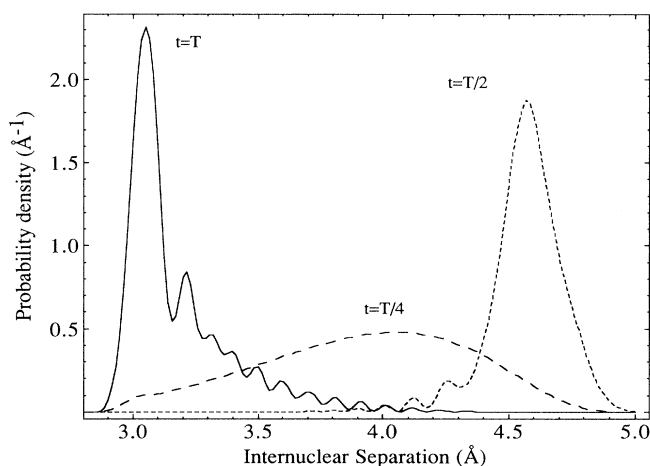

FIG. 1. The nuclear vibrational wave packet wave function generated in the $A\,^1\Sigma_u^+$ state of a sodium dimer by a 60 fs pulse of mean wavelength 630 nm. The wave function is shown for different times as a function of the vibrational period $T = 310$ fs. The wave packet is narrower than the thermal distribution at both the inner and outer turning points, and more diffuse near the potential minimum.

from the $X\,^1\Sigma_g^+$ state. A schematic showing the relevant potential energy curves of the sodium molecule is given in Ref. [12]. The source of the exciting radiation is the output of a passively mode-locked dye laser which has been amplified by a synchronously pumped dye amplifier [13]. The 4 kHz train of amplified pulses has a mean wavelength of 630 nm with 5 μJ energy and of 60 fs duration. As shown in Fig. 2, the pulses are passed through a 15 cm heat pipe at 450 °C. At this temperature the density of sodium dimers is about 10^{+15} cm^{-3}. The optical pulse is focused to a diameter of 100 μm, so that the peak intensity in the dimer sample is 40 GW/cm^2. About 20% of the ground electronic state population is transferred to the $A\,^1\Sigma_u^+$ state at this energy density.

The radiation from the heat pipe is collected from a solid angle of 0.03 sr near the direction of propagation of the exciting pulse by off-axis parabolic metal mirrors. It is focused onto a nonlinear crystal (500 μm thick beta-barium borate) coincidentally with a split-off portion (2 μJ) of the exciting pulse (which plays the role of the gate pulse) that has been delayed with respect to the portion incident on the sodium cell. The simultaneous presence of both the fluorescence and the gate pulse generates ultraviolet sum-frequency generation that is then filtered by the double-prism monochromator, and is incident on a photon-counting photomultiplier. The temporal resolution of the apparatus is about 65 fs and the spectral resolution is about 4 nm. Both the small collection angle and the use of reflective optics are necessary to minimize the group velocity dispersion that reduces the temporal resolution of the apparatus.

Results of the measurements are shown in Fig. 3, together with the calculated signal using the wave packet of Fig. 1. The wavelength indicated in each diagram is inferred from the setting of the monochromator and a measurement of the spectrum of the gate pulse.

The emission at 800 nm occurs when the wave packet is at the outer turning point. It shows modulations at an average fundamental period of 310 fs, exactly that expected of a classical vibration. The phase of the modulation peaks is also exactly what might be expected from a

classical argument; the first maximum occurs 155 fs after excitation, indicating that the nuclei take exactly one-half period to reach the outer turning point after being generated near the inner turning point. The deep modulation indicates that the detected fluorescence is predominantly that from molecules undergoing a transition between the A and X states. More importantly, it also indicates that the wave packet is very well localized—a spatially diffuse wave packet does not give rise to large fluctuations in the probability of finding the nuclei at a particular separation at different times.

When the spectrometer is tuned to a slightly shorter wavelength at 782 nm, a "splitting" of the beats is observed compared with the signal at 800 nm. As long as the spectrometer is not tuned to one of the turning points, the double beats are observed since the wave packet passes any internuclear separation twice in each oscillation. At 782 nm, the wave packet is observed as it approaches and moves away from the outer turning point.

The internuclear separation for which the position ex-

FIG. 3. The experimental and theoretical time- and frequency-resolved spectrum of spontaneous emission from the wave packet of Fig. 1. The two lines drawn through all eight figures are at times $\frac{1}{2}T$ and $\frac{3}{2}T$ where $T = 310$ fs is the vibrational period. The time gate duration is 60 fs, and the spectral filter width is 4 nm. The motion of the mean position is clear from the changing temporal structure at different detection wavelengths (shown in nm) as discussed in the text. The spatial expansion of the wave packet is evident from the decrease in overall signal amplitude as the detected wavelength is tuned away from the outer turning point to the bottom of the potential.
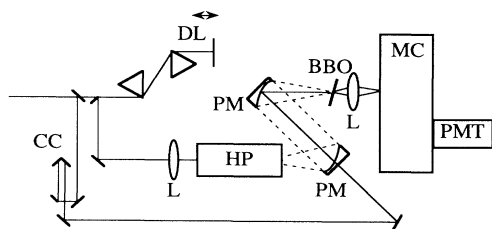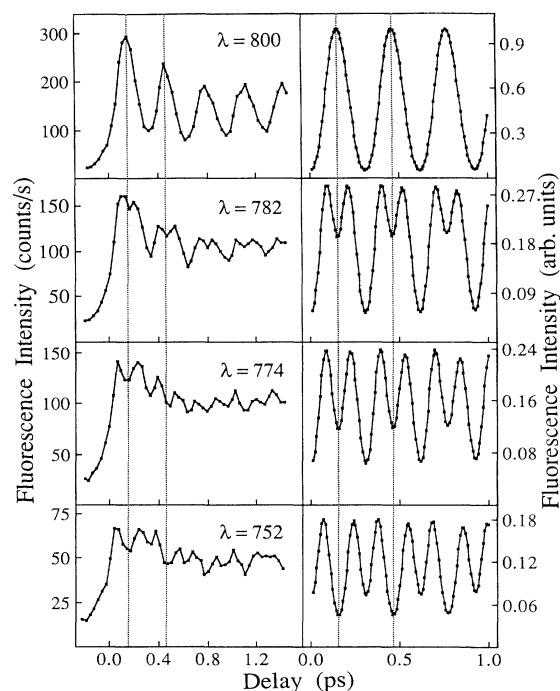

FIG. 2. A schematic diagram of the experimental apparatus. The details are discussed in the text. DL, dispersion and delay line; CC, corner cube; L, lens; HP, heat pipe containing sodium vapor; PM, off-axis parabolic mirrors; BBO, up-conversion crystal; MC, double-prism monochromator; PMT, photon-counting photomultiplier tube.

pectation value is modulated sinusoidally at twice the vibrational frequency is the separation that marks the "midpoint" of the trajectory—from this point to each of the turning points takes one-quarter of the vibrational period. From the experimental data it is clear that the midpoint of the trajectory is at 774 nm. The modulation has decreased to 20% due to both the increased dispersion of the wave packet compared with the outer turning point and the temporal resolution of our apparatus, which will reduce the modulation depths for periods of 100 fs or so. The overall signal amplitude has also decreased, due to the reduction in the peak amplitude of the state's wave function, showing that the wave packet is now more extended spatially than near the outer turning point, and to the change in Franck-Condon factors at this internuclear separation.

At yet shorter wavelengths, the temporal structure again changes to one in which there are two unevenly spaced maxima per period. The packet passes this internuclear separation twice per period, but since this point is not the midpoint of the trajectory it traverses the distance to the inner turning point and back to the detection point more quickly than via the outer turning point. At 752 nm, corresponding to internuclear separations near the minimum of the A-state nuclear potential, the modulations exhibit this temporal asymmetry. Notice that the double beats are now centered around the time delays that correspond to the minima of the signal at 800 nm. If we were able to tune the spectrometer to view the inner turning point, it is clear we would again see the modulation at the fundamental vibrational frequency; however, the peaks of the modulation would be exactly out of phase with the signal at the outer turning point. It is not possible to measure the wave packet dynamics at yet shorter wavelengths due to noise in the detection system arising from up-conversion of the gate pulse. The overall signal amplitude at 752 nm is about 5 times smaller than that at 800 nm, but the modulation depth is still about 30%. The wave packet is more localized than at the midpoint of its trajectory, but not so strongly localized as at the outer turning point.

The calculated data in Fig. 3 show the same trends as the measured signal. The anharmonicity, however, is larger in the experimental than in the theoretical data. The calculations show that the midpoint of the trajectory should occur at 763 nm whereas the experimental data indicate it is at a higher wavelength. This discrepancy could be from the use of rotationless potentials in the theoretical model.

The essential feature of the molecular system that allows such a probe is that the electronic ground state as well as the excited state have more than one level to which the nuclei may couple. For such systems the quantum beats observable in the spontaneous fluorescence are a powerful spectroscopic tool, especially for systems in which the wave packet degrees of freedom are strongly damped, because this technique does not rely on determining the revival times of the system in order to obtain the potential anharmonicity. Thus it may be useful in the study of wave packet excitations in quantum confined electronic microstructures and large molecules.

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