Experimental Determination of the Quantum-Mechanical State of a Molecular Vibrational Mode Using Fluorescence Tomography

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We present a spectroscopic method for the complete characterization of the quantum state of the vibrational mode of a molecule in terms of a phase-space quasiprobability distribution. The distribution for a molecular vibrational mode excited by a short optical pulse is reconstructed from measurements of its time-dependent spectrum of fluorescence.

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In order to make predictions about all possible expectation values of a quantum-mechanical system it is necessary to know the state of the system. The standard interpretation of quantum mechanics claims, therefore, that the density operator of the system contains all knowable information. Thus, from the very beginnings of the quantum theory, the measurability of a quantum system has been a subject of continual debate [1]. While it is well established that the wave function or density matrix of a single quantum system cannot be determined, it is possible to measure those of an ensemble of identically prepared quantum systems [2]. The recent work of Smithey *et al.* [3] in characterizing the quantum state of a light field using optical homodyne tomography is an excellent example of such a measurement. Their technique, based on a suggestion of Vogel and Risken [4], makes use of a dc balanced optical homodyne detector to measure a set of marginal distributions of the Wigner function of the radiation field. This set of functions may be inverted in a noniterative manner to yield the Wigner function itself. This function is uniquely related to the density matrix, so that a knowledge of the Wigner function is equivalent to a knowledge of the state of the system.

It seems pertinent to ask whether such reconstructions are possible for matter, and what measurements would yield the necessary set of marginal distributions. In fact the earliest attempts to answer questions about measurement of the state of a system were directed toward material and not optical systems. Royer [2] has reviewed a number of these suggestions, and provided some novel schemes. There are, however, very few experiments that have directly measured the quantum state of an atomic or molecular system [5]. In this Letter we present a novel method for measurement of the state of a diatomic molecular vibration (a quantum system with a single continuous degree of freedom) from its time-dependent spectrum of spontaneous emission.

Our method relies on the fact that a wave packet propagating in a harmonic potential moves in such a way that if the probability distribution of the particle's position at time t is $P(q,t) = |\Psi(q,t)|^2$, then at time $\pi/2\omega$ later, where ω is the angular frequency of the oscillator, it is proportional to the distribution of momentum at the original time, i.e., $P(q, t + \pi/2\omega) \propto |\tilde{\Psi}(p = 2m\omega q, t)|^2$. In fact, a measure of the position distribution at these two times is sufficient to reconstruct the wave function of the particle (in the case of a pure state), except for an overall sign ambiguity, by means of well-known algorithms of phase retrieval [6]. However, a more complete reconstruction [7] with no ambiguity is possible, that is also applicable to mixed states. The probability distributions for the particle's position at times between t and $t + \pi/2\omega$ are proportional to the modulus squared of various fractional Fourier transforms of the initial position distribution (appropriately scaled), and may be obtained from the Wigner function of the state of the particle by projections onto a set of axes that rotate at frequency ω in the phase space of the vibrational mode. A measurement of a sufficient number of these distributions of position at different times is adequate to allow reconstruction of the Wigner function through the inverse Radon transform.

The applicability of this technique relies on the ability to measure the probability distribution of the particle's position at several different times. For a diatomic molecule in an excited electronic state the light emitted when the electron returns to the ground state effectively maps the internuclear separation into wavelength [8], so that such measurements are possible in principle, but at a price. The cost of this mapping is that the position distribution function is blurred. Although there is no fundamental reason why the position distribution of a quantum-mechanical system at any given time cannot be measured with arbitrary accuracy, when the position is mapped to wavelength a problem arises, because the wavelength of the emitted radiation cannot be determined to better accuracy than the inverse of the time duration

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for which it is detected. Thus a classical logical inconsistency, as embodied in Fourier's theorem, is inserted into the problem. Consequently, we do not measure marginal distributions of the Wigner function, but of a different quantum quasiprobability distribution, in which some of the intrinsically quantum mechanical features of the states are not so evident as in the Wigner distribution. It is still the case, however, that from the set of measured emission spectra we are able to determine a particular quasiprobability distribution that is uniquely related to the density matrix for the system.

The measured time-dependent spectra are equivalent to a set of projections of a particular quasiprobability distribution on a number of different axes in the phase space of the vibrational mode. Thus the spectra, together with a knowledge of a mapping of the emission wavelength to internuclear separation obtained from the known molecular potentials and the experimental configuration, allow one to use the inverse Radon transform to obtain the quasiprobability distribution. We therefore refer to this technique as molecular emission tomography (MET).

To establish the connection between the measured spectra and the projections of this appropriate distribution function, we make use of the Cahill-Glauber s-parametrized quasiprobability distributions [9] for a single degree of freedom, defined by

$$P_s(p,q;T) = \int d\mu \int d\nu\, e^{i\mu p + i\nu q} \times \mathrm{Tr}[\hat{\rho}(T) e^{-i\mu\hat{p} - i\nu\hat{q}}] e^{s(\mu^2+\nu^2)/4}, \quad (1)$$

where $\hat{\rho}(T)$ is the density operator for the system at time T, and $\hat{p}$ and $\hat{q}$ are (dimensionless) position and momentum operators. For $s = 0$, $P_s(p,q;T)$ is the Wigner function, whereas for $s = -1$ it is the Q function or Husimi distribution. These are both related to the density matrix for the state in a straightforward manner [9], although it is easier in practice in the presence of noise to obtain the density matrix from the Wigner function than the Q function.

The detected spectra are related to one of these functions with a value of s that is determined by the particular experimental arrangement. In order to understand this, it is necessary to define the notion of a time-dependent spectrum, using the ideas developed by Eberly and Wodkiewicz [10]. In our experiments, the fluorescence from the excited molecules is first sampled by a time gate, which is opened at time T after the excitation of the wave packet, for a duration Γ^{-1}, and then frequency filtered through a spectrometer with a passband γ centered at optical frequency Ω, before it is incident on a square-law integrating photodetector [8]. The detected spectrum $S(\Omega,T)$ may be written in terms of the overlap between the distribution and a "window" function $O_s(p,q;\Omega)$, for $\Gamma/\omega \gg 1$,

$$S(\Omega,T) = \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dq\, O_s(p,q;\Omega) P_s(p,q;T), \quad (2)$$

where

$$O_s(p,q;\Omega) = \int dt \int dt' \int dt''\, F(t,t',t'';\Omega) \times \int d\mu \int d\nu\, e^{i\mu p + i\nu q} \times \mathrm{Tr}[\hat{O}(t'-t'') e^{-i\mu\hat{p} - i\nu\hat{q}}] e^{-s(\mu^2+\nu^2)/4}. \quad (3)$$

This window function is closely related to the "snapshot window function" introduced by Yan *et al.* [11] and is a representation of the operator

$$\hat{O}(t'-t'') = e^{-i\hat{H}_e(t'-t'')/\hbar} e^{i\hat{H}_g(t'-t'')/\hbar}, \quad (4)$$

where $\hat{H}_e$ and $\hat{H}_g$ are the adiabatic Hamiltonians of the molecular vibrational mode in the excited and ground electronic states, respectively. The function

$$F(t,t',t'';\Omega) = H^*(t-t';\Omega,\gamma) H(t-t'';\Omega,\gamma) \times B^*(t';T,\Gamma) B(t'';T,\Gamma) \quad (5)$$

contains the response functions of the time gate, $B(t;T,\Gamma)$, and spectral filter, $H(t;\Omega,\gamma)$.

The window function may be evaluated analytically for the case where both vibrational potentials are harmonic with the same fundamental frequency but displaced equilibria; the temporal filter response function is Gaussian and the spectral filter has a narrow passband ($\gamma/\Gamma \ll 1$). In that case,

$$O_s(p,q;\Omega) = \exp\left\{-\frac{[q - Q(\Omega)]^2}{(\Gamma/\kappa\omega)^2 + s}\right\}, \quad (6)$$

where $Q(\Omega) = (\Omega - \kappa^2\omega)/\sqrt{2}\kappa\omega$ is the mapping of position to emitted frequency, and κ is the ratio of the displacement of the potential minima to the vibrational ground state width. Considered as a function of s, this set constitutes a delta sequence, so that in the limit that s tends to $s_m = -(\Gamma/\kappa\omega)^2$, this function becomes effectively a delta function mapping a specific frequency of the emitted radiation to a particular internuclear separation. Then it is clear that the detected spectra are marginal distributions of the quasiprobability distribution $P_{s_m}(p,q;T) = P_{s_m}(p\cos\omega T - q\sin\omega T, q\cos\omega T + p\sin\omega T; 0)$,

$$S(\Omega,T) = \int_{-\infty}^{\infty} dp\, P_{s_m}(p\cos\omega T - Q(\Omega)\sin\omega T, Q(\Omega)\cos\omega T + p\sin\omega T; 0). \quad (7)$$

Given a set of detected spectra for different values of T between π/ω and $-\pi/\omega$, Eq. (7) may be inverted to yield the distribution $P_{s_m}(p,q;0)$ using the inverse Radon transform. For a finite set of T values, the inversion may be accomplished with techniques familiar in computer-assisted tomography. Specifically, we utilize the filtered backprojection algorithm for parallel-beam sampling geometry [12].

The reconstruction of $P_s(p,q)$ for a real molecule, in which the vibrational potentials are not harmonic, poses some problems. In this case the window function does not have such a simple analytic form, and further approximations are necessary. First, it is necessary to generate maps of sampling time T to the phase-space rotation angle, and of internuclear separation q to frequency Ω. Second, it is necessary to assume that $P_s(p,q)$ does not change in shape significantly during a single period of its trajectory. The frequency map may be generated by calculating the average value of $q = \bar{q}$ of the window function for a given frequency. For our experiments, we approximate the temporal map as a harmonic one, and assume that the probability distribution remains undistorted for a single period. We refer to this set of assumptions as the "harmonic approximation." Note that is not necessary to assume that $P_s(p,q)$ never changes shape, only that it is constant during the single period for which the spectra are measured. Thus, it is tantamount to an assumption of weak anharmonicity in the case of a well-localized wave packet, or simply the excitation of a wave packet that is a coherent superposition of only a few levels. Moreover, it is not a severe restriction for most experiments, because it is the regime in which the wave packet does not breakup in a single period of the equivalent classical system that is precisely the regime of interest. Figure 1 illustrates the application of this technique to reconstructing the Q function of the vibrational mode of a real molecule (Na$_2$). It shows $P_{s=-1}(p,q)$ calculated for a wave packet generated in the A state of the dimer, and its reconstruction from a set of theoretical fluorescence spectra. The window function was calculated using the known vibrational potentials and assuming a Gaussian functional form for $B(t)$, with full width at e^{-1} of the maximum height (FWe^{-1}M) equal to that of the experimental gate pulses.

Our experimental arrangement is identical to that outlined in Ref. [13], and is shown schematically in Fig. 2. It consists of a heat pipe containing sodium dimers at a density of approximately 10^{13} cm^{-3}, which are illuminated by a 4 kHz train of optical pulses with 5 μJ energy and 60 fs duration with mean wavelength of 630 nm. The fluorescence from this sample is collected by off-axis parabolic metal mirrors and focused synchronously with a split-off portion of the exciting pulse (which plays the role of the time-gate shutter) onto a nonlinear crystal (500 μm thick beta-barium borate). The resulting ultraviolet sum-frequency radiation is then filtered by a double-prism monochromator and detected by a photon-counting photomultiplier. The temporal resolution of this apparatus is about 65 fs. The exciting pulse generates a vibrational wave packet in the $A^1\Sigma_u^+$ state of the sodium dimer, which undergoes a periodic evolution with period of 310 fs. The time-dependent spectra are measured by selecting a particular wavelength on the monochromator and then scanning the gate pulse over a delay equal to one period of the wave packet's motion. A complete picture of the evolving emission spectrum over the period is builtup by making scans for several different settings of the monochromator.

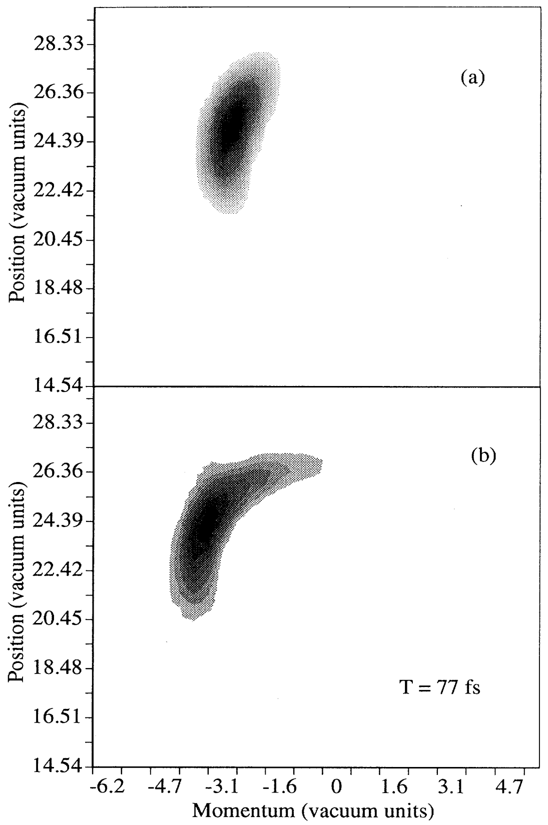

FIG. 1. (a) The theoretical quasiprobability distribution $P_{-1}(p,q)$ for a wave packet excited in the vibrational mode of a sodium dimer by a 60 fs duration, transform-limited Gaussian pulse. The approximate dimensionless displacement κ is 1.7. (b) Tomographic reconstruction of the distribution from calculated time-dependent emission spectra, using the harmonic approximation.

In Fig. 3 we show quasiprobability distributions for a wave packet in sodium, obtained by tomographic reconstruction from a measured set of emission spectra. There

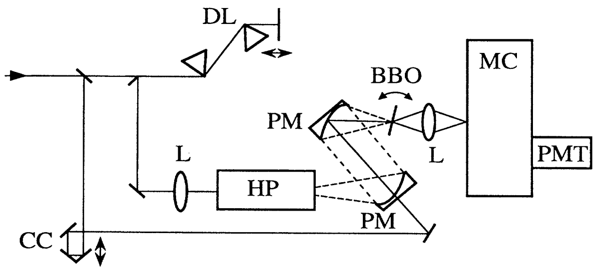

FIG. 2. Experimental apparatus for measuring the time-dependent spectrum of fluorescence from a sample of excited molecules. (HP): heat pipe; (DDL): dispersive delay line; (CC): movable corner cube; (L): lens; (PM): off-axis parabolic metal mirrors; (BBO) nonlinear crystal for upconversion; (MC): monochromator; (PMT): photon-counting photomultiplier.

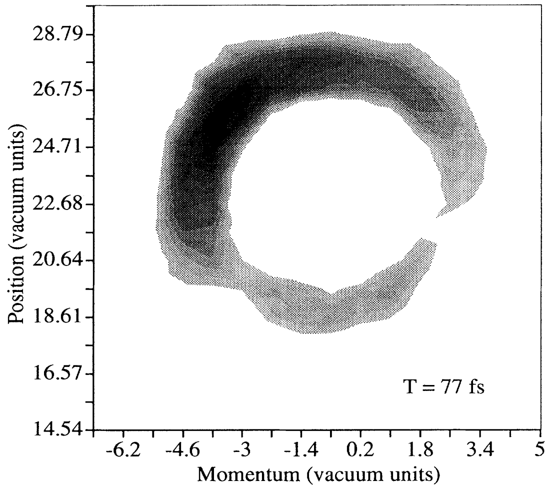

FIG. 3. Tomographic reconstruction of a quasiprobability distribution from the experimentally measured time-dependent fluorescence spectra. The time gate duration was 65 fs, which implies $s = -0.8$.

is reasonable agreement between the tomographically inverted function and the calculated function [Fig. 1(b)], in terms of the shape, location, and size of the distributions. There is not perfect agreement, however. In certain regions of the phase space the function reconstructed from the experimentally measured spectra is negative, for example, and has an extended annular component. This is primarily due to the time- and frequency-independent background signal in each of the spectra. The reconstruction procedure interprets this signal as arising from any time-stationary state, such as an eigenstate of the vibrational Hamiltonian, thus leading to a delocalized, and nonpositive, phase-space distribution. A further limitation on the accuracy of our measured distributions is the small number of data points since, even if $P_s(p,q)$ is approximately Gaussian, some 27 values of T and 64 values of wavelength per spectrum are required for accurate reconstruction [3]. From sufficiently accurate measurements of $P_s(p,q)$, it is possible to obtain the density matrix or wave function directly [9], using similar methods to those of Smithey *et al.* [14].

We note that some information about the molecular potentials is needed for fluorescence tomography to work, so that the window function may be determined. This method could also be applied to absorption measurements, with the caveat that it is necessary to know the state of the final electronic-vibrational system in order to perform the reconstruction uniquely.

In conclusion, we have shown that molecular emission tomography can be used to measure a quantum quasiprobability distribution of the vibrational mode of a molecule. This distribution is related uniquely to the density matrix, and with this in hand one could, in principle, calculate any one-time expectation value for the oscillator. We emphasize that the success of the method is predicated upon the ability to measure the spectrum of fluorescence from the molecule at many different times, and thus the marginal distributions of the function $P_s(p,q)$ for many different orientations of the phase space coordinates. Previous experiments have measured the time-dependent absorption or laser-induced fluorescence from molecular wave packet states at only one or two wavelengths [15]. Such restricted measurements contain insufficient information to completely characterize the quantum state. Techniques such as those demonstrated here are necessary in order to get full quantum information, even for stationary states. Aside from the implications for measurement of novel quantum-mechanical states of matter, our technique provides an important tool for the experiments in quantum control. To date in such experiments the generated wave packets have been calculated from inferred exciting-pulse shapes. Direct measurement of the wave packet provides a useful counterpoint, especially in the regime of strong-field excitation.

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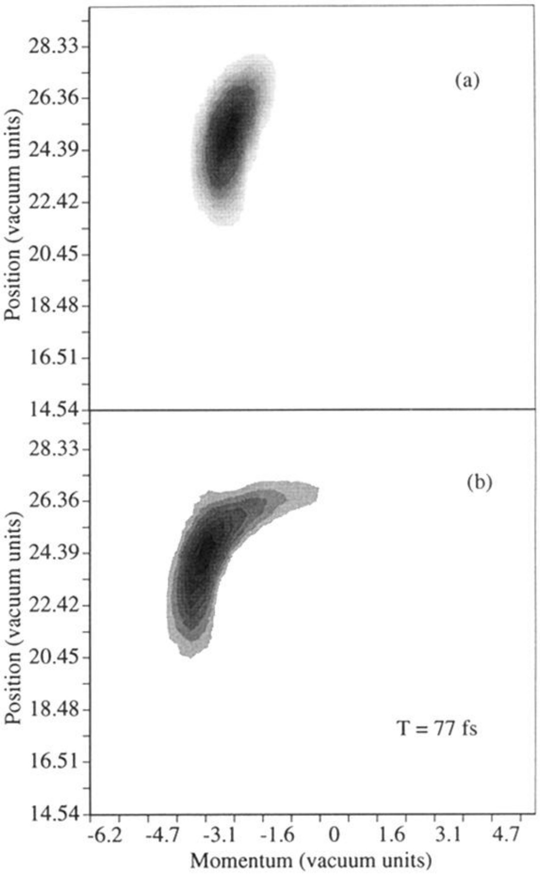

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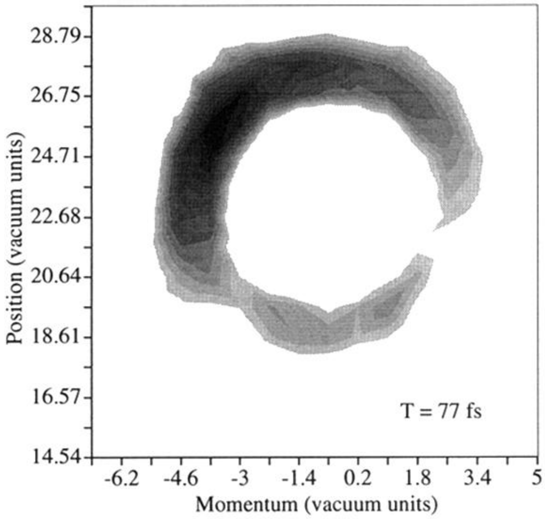

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