Observation of single molecule transport at surfaces via scanning microscopies: Monte Carlo wave function study of a model problem

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We discuss experiments where the trajectories of individual molecules or atoms at surfaces are observed by means of scanning microscopy. A scanning probe moves along the surface and excites the molecule so that the molecule's location is deduced from the times at which fluorescence photons are emitted. Operation of other types of scanning microscopes can be described by similar models. The observed trajectories are inherently affected by the interaction between the molecule and the probe such that the measured diffusion coefficient depends on the frequency at which the surface is scanned. The number of photons emitted by the molecule during a scan is affected in a nontrivial way by its mobility. If photoexcitation increases the mobility, we find emission to be suppressed.

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I. INTRODUCTION

A variety of experimental techniques have emerged during recent years, allowing one to locate, monitor, and manipulate individual atoms and molecules [1–6]. Examples include single molecule optical spectroscopy, scanning tunneling microscopy, and atomic force microscopy. As the spatial and temporal resolution improves, one eventually gets to the limit where the quantum properties of the observed molecules and their interactions with the probing device can no longer be ignored.

In a recent study, Lauhon and Ho [7] observed tunneling of single hydrogen atoms at a surface using a scanning tunneling microscope (STM). The possibility to observe a single particle undergoing quantum transitions poses a number of conceptual questions. What is the actual information about the single quantum system that is revealed by such measurements? What is the meaning of the measured ''trajectory''? The wave function (or the density matrix) of a molecule describes the probability to find it in any given state. Thus locating the molecule is a stochastic process. Solving the Schrödinger equation is not sufficient to describe such experiments: this has to be supplemented by a Monte Carlo procedure to simulate the detection process.

Another unusual aspect of single molecule experiments is that the interaction of the molecule with the detector cannot be neglected. For example, suppose we are monitoring a single atom by exciting it with a laser and detecting fluorescence photons it emits. The photon flux arriving at the detector depends on the laser intensity and on the emission rate. The time resolution of a single atom trajectory measured in this way cannot be better than the duration of the excitation-emission cycle, τ. The more closely we would like to watch the atom, the shorter τ must be. Shorter τ means stronger interaction of the atom with the laser field as well as with the vacuum electromagnetic field. Emission automatically causes decoherence. Therefore if we monitor the atom over a time longer than the emission time then we cannot neglect this decoherence caused by the interaction with the vacuum field.

This picture is very different from that of ultrafast time resolved spectroscopies of bulk materials, which are usually carried out at time scales much shorter than emission times. Decoherence due to the interaction with the vacuum field has negligible effect on the molecules' dynamics in this case.

Interaction with the detector sometimes provides a useful way of manipulating single molecules. For example, Ho's group has used the interaction of the STM tip with molecules adsorbed at surfaces to dissociate, rotate, or vibrationally excite the molecules [8–10].

The purpose of this paper is to understand the meaning and the properties of single molecule trajectories as measured by scanning microscopy. The topic of ''quantum trajectories'' has previously been discussed by Marksteiner, Ellinger, and Zoller [11] in the context of quantum diffusion in optical molasses. Those authors devised a measurement scheme in which the location of an atom is measured by angle resolved detection of the emitted photons. The simulated atomic trajectories exhibit unusual properties such as anomalous diffusion. The spatial resolution provided by such a scheme is limited by the laser wavelength. In contrast, the scanning microscopy approach (e.g., near field scanning optical microscopy) does not have such a limitation.

Thus the physical situation studied here differs from that of Ref. [11]. Our model (Sec. II) describes a fluorescence excitation experiment, in which the molecule adsorbed at a surface is located by exciting it with a spatially localized electromagnetic field (possibly in a near field setup) and monitoring its fluorescence. The location of the molecule is deduced from the position of the probe (i.e., the field) at the time at which a fluorescence photon is detected. Unlike in the case studied in Ref. [11], the direction of the emitted photons is not resolved in our scheme. Our scheme thus exploits the mapping between the times when photons are detected and the observed trajectory of the molecule. The properties of the molecule's dynamics (such as its diffusion coefficient) are intimately related to the photoemission statistics. The statistics of light emitted by single molecules has recently become a subject of intense study [2,12–18].

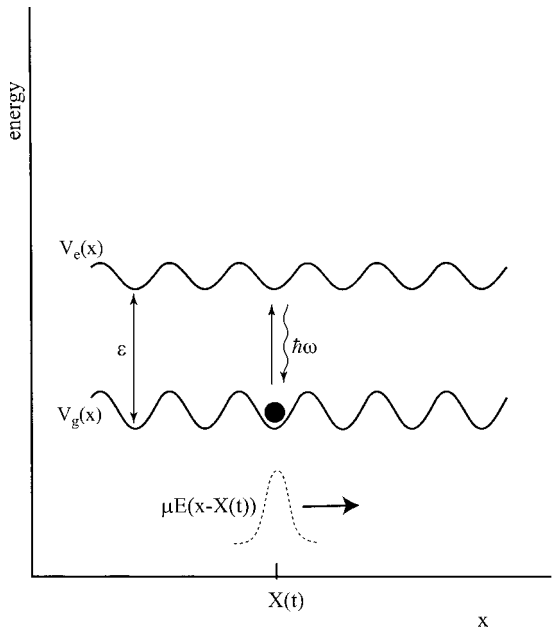

FIG. 1. The energy of the molecule-surface interaction in the ground and excited electronic states. Also shown is the interaction energy between the laser and the molecule when the probe is located at $X(t)$.

While details might be different, our model is rather generic and captures the essential properties of most scanning microscopies. The molecule can move (either by tunneling or thermal hopping) during the experiment and our aim will be to describe the characteristics of this motion (diffusion coefficient, etc.) as observed in such an experiment.

In Sec. III we will provide a summary of the Monte Carlo wave function method used to numerically simulate the dynamics of our model. In Sec. IV, we will examine the deep quantum limit, in which the molecule's dephasing time, in the absence of the probing laser, is longer than the duration of the experiment. In this limit, the only source of dephasing is the instrument itself. As a consequence, the molecule stays coherent until it emits a photon, and therefore its diffusion coefficient measured in such an experiment will turn out to depend on the rate at which the surface is scanned. We will argue that this kind of experiment can be performed with cold atoms in optical lattices, where the dephasing times are very long. We will also see that other dephasing mechanisms change this picture and lead to a diffusion coefficient that is independent of the scanning rate.

In Sec. V we will explore whether or not the emission signal from a single molecule is enhanced by its diffusion. We will also examine the effect of photoinduced diffusion. Section VI concludes with closing remarks.

II. THE MODEL

Our model is schematically shown in Fig. 1. We consider a molecule (or atom) of mass m moving in a periodic multiwell potential along x that mimics a one-dimensional ''surface.'' The molecule has two electronic states, $|g\rangle$ and $|e\rangle$, with energies ε_e and ε_g, and is excited by a resonant electromagnetic field at a frequency $\omega=\varepsilon\equiv\varepsilon_e-\varepsilon_g$. The amplitude of the field is given by $E(x-X(t))$, a function that is spatially localized around the position of the probe $X(t)$ (Fig. 1). We will assume that the spatial width of $E(x)$ is comparable to the size of the single well. The Hamiltonian is:

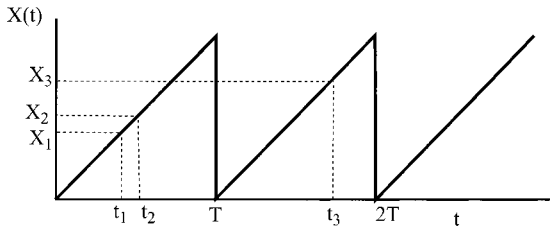

FIG. 2. The position of the probe $X(t)$ as a function of time. If photons are detected at times t_1, t_2, and t_3, we say that the molecule was found at X_1, X_2, and X_3 at these times.

$$H=[V_g(x)+p^2/2m]|g\rangle\langle g|+[\varepsilon+V_e(x)+p^2/2m]|e\rangle\langle e| - \mu E(x-X(t))\cos(\omega t)[|g\rangle\langle e|+|e\rangle\langle g|]. \quad (1)$$

The last term in Eq. (1) describes the dipole interaction of the molecule with light. Classically, if the position of the probe $X(t)$ is close to the molecule's position x then the field can resonantly excite the molecule and the molecule can emit a photon. Therefore if we register a photon at time t_1 then we know that the molecule is located at $X(t_1)$ (see Fig. 2). The accuracy of the measurement is limited by the width of the envelope $E(X(t)-x)$ and also by the fact that the molecule and/or probe can move during the lifetime of the excited state of the molecule. The position of the probe $X(t)$ is a periodic function of time as shown in Fig. 2. The total time of the scan is T and the time the probe spends at each well is $t_{\text{probe}}=T/N$ where N is the number of wells. We will assume periodic boundary conditions for the periodic multiwell potentials $V_g(x)$ and $V_e(x)$ so that the total number of distinct wells is N. We use $N=40$ in all simulations. The excited molecule will generally have a different charge distribution from that in the ground state and therefore it will interact with the surface differently. As a consequence, the excited state potential $V_e(x)$ generally differs from the ground state potential $V_g(x)$.

Besides interacting with the surface and with the laser probe, the molecule may also be coupled to a continuum of surface modes (phonons or electronic excitations) that provide an additional mechanism for dephasing and energy relaxation. Those will be treated here in a phenomenological fashion, using a Monte Carlo wave function approach. For a review and relevant references see Ref. [19]. Our particular implementation of the algorithm and the method in which we treat dephasing are given in Ref. [20].

To simplify the numerical treatment of the Hamiltonian of Eq. (1) I will use two approximations:

(a) Rotating wave approximation [21]. In the rotating frame, the Hamiltonian (1) takes the form:

$$H=[V_g(x)+p^2/2m]|g\rangle\langle g|+[\varepsilon-\hbar\omega+V_e(x)+p^2/2m]|e\rangle \times\langle e|-\hbar\Omega(x-X(t))[|g\rangle\langle e|+|e\rangle\langle g|], \quad (2)$$

where

$$\hbar\Omega(x-X(t))=\mu E(x-X(t))/2 \tag{3}$$

can be thought of as a Rabi frequency operator that depends on the positions of both the probe and the molecule.

(b) Tight binding approximation. The energy levels in the periodic potentials form bands. For both V_g and V_e, we will neglect all bands but the lowest ones. This implies that the following replacement is made:

$$V_{g(e)}(x)+p^2/2m \rightarrow -\sum \Delta_{g(e)}(|n\rangle\langle n+1|+|n+1\rangle\langle n|). \tag{4}$$

Here $|n\rangle$ is a state that is localized in the nth well and $\Delta_{g(e)}$ is the tunneling matrix element between two neighboring wells for a particle in the potential $V_{g(e)}$. There are a total of N wells and periodic boundary conditions are assumed. In addition, the Rabi frequency operator (which is diagonal in x) is replaced by $\hbar\Omega(x-X(t)) \rightarrow \hbar\Omega\,\delta_{n,X(t)}|n\rangle\langle n|$ where $\delta_{nm}=1$ if $n=m$ and zero otherwise. Since we have replaced the continuous coordinate x by the discrete well number n, we also modify $X(t)$ such that it can only take discrete values: $X(t)=[Nt/T] \pmod N$ where $[a]$ indicates the smallest integer greater than or equal to a. One should be aware that by making the tight binding approximation we have discarded some interesting phenomena [such as over-barrier transitions in the potential $V_g(x)$, the energy for which being provided by the atom recoil in photoemission [11]].

If x is taken to be an angular variable, the Hamiltonian (1)–(4) can be used to describe rotations of a molecule. A Hamiltonian of this type seems suitable to describe the experiments [10] where rotations of a single molecule are excited by an STM tip.

Note that the Hamiltonian (1) describes a periodically driven particle in a periodic potential. It is similar to the Hamiltonian of a periodically kicked rotor [22] except that the ''kicking'' is provided by a time dependent coupling between the ground and excited states caused by an electromagnetic field and that there is an additional constant angular potential. A physical example of such a rotor could be a CH_3 group rotating around the bond connecting it with the rest of the molecule. In this case the potential $V_{g(e)}$ would be threefold. In view of the above similarity, it is not unexpected to find (see Sec. III) a phenomenon that is similar to the ''measurement-induced'' diffusion described in Ref. [22].

III. MONTE CARLO WAVE FUNCTION ALGORITHM

We use the Monte Carlo wave function (MCWF) approach [19,20,23–27] to study the dynamics of our model. For details of this approach see the cited literature. Here we give a very brief summery of the method.

It is assumed that the evolution of the molecule's density matrix ρ is described by

$$d\rho/dt=-i[H,\rho]-R\rho, \tag{5}$$

where H is the Hamiltonian defined by Eqs. (1)–(4) and R is an operator that contains effects of relaxation and dephasing so it can be written as a sum of two terms:

$$R=R_r+R_d. \tag{6}$$

The dephasing part has the following matrix elements:

$$\langle n,\sigma|R_d\rho|n',\sigma'\rangle=\gamma_{n\sigma n'\sigma'}\langle n,\sigma|\rho|n',\sigma'\rangle,$$

$$\gamma_{n\sigma n'\sigma'}=\gamma+\Gamma(\delta_{\sigma,e}+\delta_{\sigma',e})/2, \tag{7}$$

where $\sigma=e$, g and $n\neq n'$ and/or $\sigma\neq\sigma'$. The dephasing rate $\gamma_{n\sigma n'\sigma'}$ describes how fast the coherence is lost between any pair of distinct states and is the sum of a pure dephasing rate γ (which is assumed here to be the same for all states) and a contribution caused by emission and proportional to the emission rate Γ.

The relaxation part of R is diagonal:

$$\langle n,e|R_r\rho|n,e\rangle=\Gamma\langle n,e|\rho|n,e\rangle,$$

$$\langle n,g|R_r\rho|n,g\rangle=-\Gamma\langle n,e|\rho|n,e\rangle. \tag{8}$$

In our model, photoemission is the only source of relaxation. Additional relaxation mechanisms such as those due to coupling to phonons or other excitations can be easily included within our formalism if desired.

Equation (5) can be solved directly. Calculating the emission statistics would then involve tedious computation of correlation functions of the dipole operator from Eq. (5). The MCWF algorithm [11,19,20,23–27] offers an equivalent yet more convenient approach to the photocounting statistics. Specifically, one constructs a fictitious wave function

$$|\psi(r)\rangle=\sum_{n,\sigma} c_{n,\sigma}(t)|n,\sigma\rangle.$$

''Coherent'' evolution of this wave function (which, in the MCWF context, is free propagation under an effective, R-dependent Hamiltonian [19,20,23–27]) is interrupted by stochastic jumps whose probabilities are determined by the operator R. After each photoemission jump the wave function is reset to $|\psi\rangle=|n,g\rangle$, i.e., becomes localized in a well. In addition to the ''photoemission jumps,'' the algorithm includes ''collisions,'' which randomize the phase of the wave function. The latter are necessary to describe the pure dephasing [20]. The algorithm has the following two properties.

(i) The evolution of the density operator $\overline{|\psi(t)\rangle\langle\psi(t)|}$ averaged over runs of this stochastic algorithm is identical to that of the density matrix $\rho(t)$ under Eq. (5).

(ii) The statistics of the ''photoemission jumps'' generated by this algorithm are precisely the same as the statistics of the photons emitted by the molecule if its density matrix satisfies Eq. (5) [19,23–25]. The second property allows us to carry out our ''scanning microscopy'' on a computer by generating times at which photons are emitted.

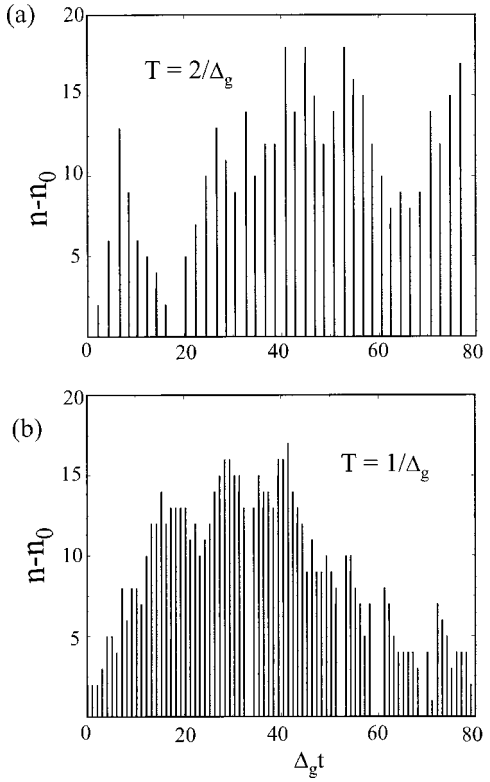

FIG. 3. The measured position of the molecule as a function of time for two different values of the scan time. The parameters used in the simulation are $\gamma=0$, $\Gamma=100\,\Delta_g$, $\Omega=80\,\Delta_g$, and $\Delta_e=\Delta_g$.

IV. MEASURING THE DIFFUSION COEFFICIENT

Thinking classically, when the probe passes over the well containing the molecule, one will detect a burst of fluorescence photons emitted by the molecule. We will assume that the excitation lifetime $1/\Gamma$ (where Γ is the emission rate) is shorter than the time $t_{\text{probe}}=T/N$ the probe spends at each well so that more than one photon will be typically emitted. If such a burst is detected around time t_1 then we say we have found our molecule at position $n_1=X(t_1)$. Once the probe has moved away from the molecule's location, no photons will be detected until a later time t_2. This new emission time is close to t_1+T, assuming that the molecule cannot move too far from n_1 during the scan time T. If there is no motion, i.e., $\Delta_g=\Delta_e=0$, then the molecule will be found at t_2 at the same position n_1. However, for nonzero Δ_g and Δ_e we may find the molecule at a different location $n_2\neq n_1$. Figure 3 shows the result of a MCWF simulation of this process. Each spike in Fig. 3 corresponds to a burst of photons (the resolution of the plot is not sufficient to see individual photons). The spikes are separated by a time close to the scan period T. The height of the spike is equal to the displacement $n-n_0$ of the molecule (measured as described above) relative to its initial position n_0 where the molecule was initially placed (that is, the molecule's density matrix was equal to $|n_0\rangle\langle n_0|$ in the beginning of the simulation). The two plots in Figs. 3(a) and 3(b) correspond to two different scan periods T: $T=2/\Delta_g$ and $T=1/\Delta_g$, respectively. The process $n(t)$, with $t\approx 0,T,2T,\ldots$, is diffusion. That is, the mean square displacement is proportional to time: $\langle[n(t)-n_0]^2\rangle=Dt$. This, of course, cannot be ascertained by examination of Fig. 3 but can easily be checked by repeating the simulation and computing the average. However, an unusual feature of Fig. 3 is that the diffusion coefficient D in Fig. 3(a) is different from that in Fig. 3(b). Simulations show that the diffusion coefficient in Fig. 3(a) is twice that in Fig. 3(b). Thus the diffusion coefficient depends on the scan time T.

This finding could be anticipated from the following heuristic arguments. We first note that coherent tunneling of the molecule is not a diffusion process. To see this, suppose that there is no laser field and no emission. In the limit $N\to\infty$ this case can be solved analytically. If we start with $|\psi(0)\rangle=|n_0\rangle$, compute $|\psi(t)\rangle=\exp(-iHt)|n_0\rangle$, then we will find that the mean square displacement of the molecule at time t is given by

$$\langle(n-n_0)^2\rangle\equiv\sum_n\,(n-n_0)^2|\langle n|\psi(t)\rangle|^2$$

$$=\sum_n\,(n-n_0)^2J^2_{n-n_0}(2t\Delta_g)=2\Delta_g^2t^2,$$

where $J_n(x)$ stands for the Bessel function. This is a ballistic, not diffusional, regime known in quantum diffusion theory [28–30]. If we neglect any decoherence effects during the time between two bursts of photons then we will find that the mean square displacement between two spikes in Fig. 3 should be proportional to T^2. However, the coherent propagation process is disrupted every time a photon is registered. In quantum measurement theory this is referred to as ''the collapse of the wave function.'' In the MCWF algorithm, such collapse takes place each time a photoemission jump resets the wave function to $|\psi\rangle=|n_1,g\rangle$, n_1 being whatever value that has been registered by the scanning microscope. Until the next burst of photons, the molecule's wave function undergoes coherent propagation with the new initial condition $n=n_1$, until the next burst of photons arrives, locating the molecule at a new position n_2. The molecule's position $n_0,n_1,n_2,\ldots$, measured in successive scans undergoes a diffusion process. The displacements $n_1-n_0,n_2-n_1,\ldots$, are independent of one another, with the mean square displacement being $\langle(n_k-n_{k-1})^2\rangle=2\Delta_g^2T^2$ and $\langle n_k-n_{k-1}\rangle=0$. From this we find

$$\langle(n_k-n_0)^2\rangle=k\langle(n_k-n_{k-1})^2\rangle=2\Delta_g^2\,\mathrm{Tt}$$

since $k\sim t/T$. Thus the diffusion coefficient is proportional to T. Note that this finding may be regarded as a manifestation of the quantum Zeno effect [31–33]. As $T\to 0$, the diffusion coefficient approaches zero so the molecule is no longer seen to move. However, our results cannot be extrapolated to the limit $T\to 0$ because the interaction time $t_{\text{probe}}=T/N$ must be long enough to ensure that the molecule can be excited and thus detected.

The picture suggested by the above argument is that the molecule undergoes undisturbed coherent evolution between the bursts (during which the mean square displacement is

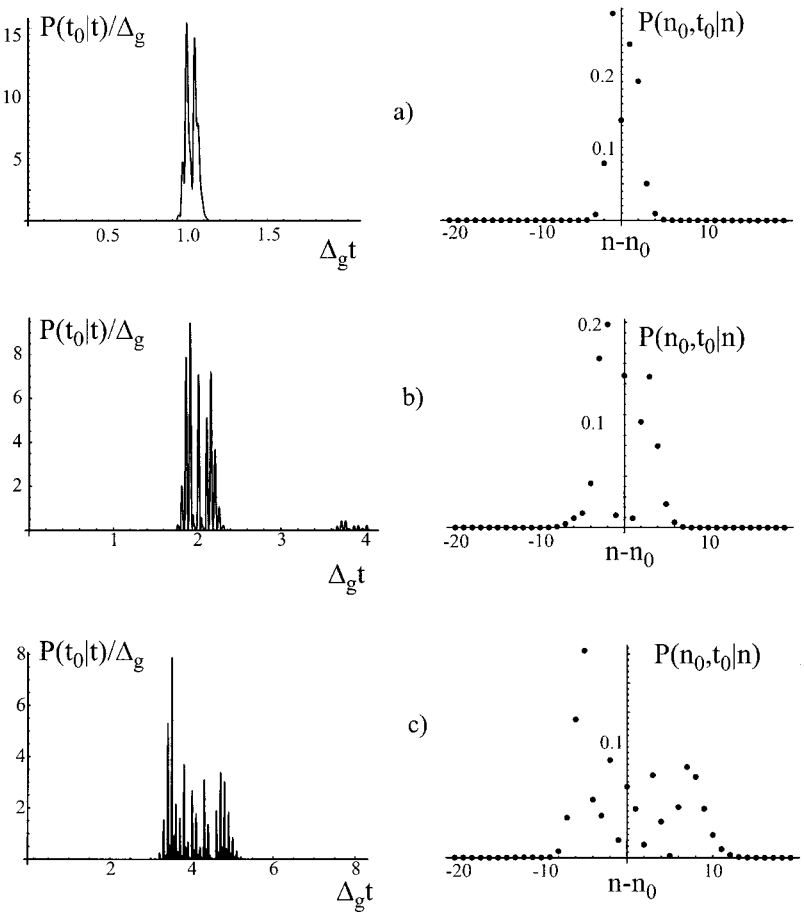

FIG. 4. Probability distributions $P(t_0|t)$ and $P(n_0|n)$ for three different values of the scan time T. (a) $T=1/\Delta_g$; (b) $T=2/\Delta_g$; (c) $T=4/\Delta_g$. Other simulation parameters are $\gamma=0$, $\Gamma=100\,\Delta_g$, $\Omega=80\,\Delta_g$, $\Delta_e=\Delta_g$, and $t_0=t_{\mathrm{probe}}$.

proportional to t^2) and the coherence is disrupted each time the molecule is located by the probe.

To understand the properties of the observed process in more detail, we now study the conditional probability $P(t_0|t)$ that a photon is detected at time t provided that the previous photon arrived at t_0. Because our Hamiltonian (1)–(4) is time dependent, this probability depends not only on the separation between the two photons but also on the time t_0 the first photon has been detected. If we choose $t_0=t_{\mathrm{probe}}=T/N$ then the first photon is emitted just at the time when the probe leaves the first well. We then expect that the next photon will most likely be emitted at a time close to $t\approx t_0+T$. If this were a precise equality, $t=t_0+T$, this would imply that the molecule would be detected at the same well $(n=1)$ where it was found at $t=t_0$. Using the time dependence of the probe position, $X(t)=[Nt/T]$, it is easy to convert the probability distribution $P(t_0|t)$ into $P(n_0,t_0|n)$, the conditional probability that the molecule is located in well number n provided it has previously been found in well $n_0=n(t_0)$ at time t_0. Figure 4 shows both these distributions for $T=1/\Delta_g$, $2/\Delta_g$, and $4/\Delta_g$. The sharp peaks in the distribution $P(t_0|t)$ are due to the coherent nature of laser excitation: the population of the excited state is an oscillatory function of time so that the emission probability has a maximum at certain times. As T is increased, the uncertainty in the arrival time t of the next photon [i.e., the spread of the distribution $P(t_0|t)$ as a function of t] becomes larger. Therefore the uncertainty in the location $n(t)$ where the molecule will be detected also increases. This is seen in the plot of $P(n_0,t_0|n)$ as a function of $n-n_0$.

The spread in $n-n_0$ tells us how much, on the average, the molecule can move during the dark time when the probe is not exciting the molecule. To quantify this, we plot the mean spread, $\langle(n-n_0)^2\rangle^{1/2}$, as a function of T in Fig. 5. For a molecule that undergoes classical diffusion, this would be proportional to $T^{1/2}$. However, what we see in Fig. 5 is ballistic transport, with

$$\langle(n-n_0)^2\rangle^{1/2}\propto T.$$

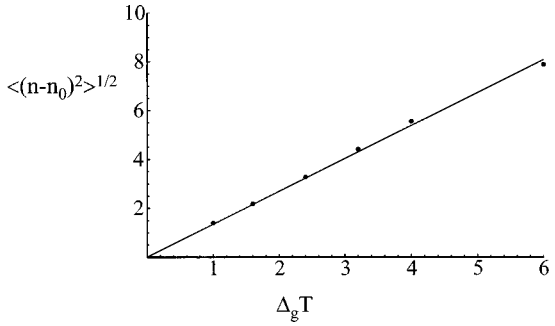

FIG. 5. The root mean square distance traveled by the molecule between two successive encounters with the probe plotted as a function of the scan time T. The parameters of the simulation are $\gamma=0$, $\Gamma=200\,\Delta_g$, $\Omega=160\,\Delta_g$, and $\Delta_e=\Delta_g$.

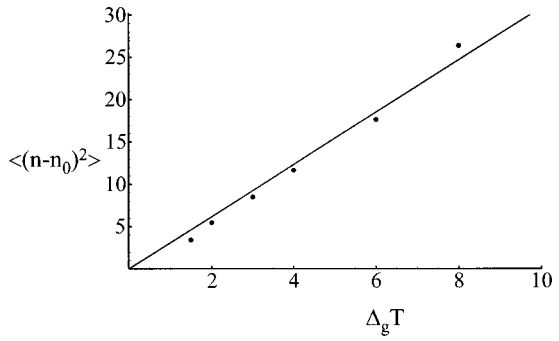

FIG. 6. The mean square distance traveled by the molecule between two successive encounters with the probe plotted as a function of the scan time T. The parameters used in the simulation are $\gamma=\Delta_g$, $\Gamma=100\,\Delta_g$, $\Omega=80\,\Delta_g$, and $\Delta_e=\Delta_g$. Note that the quantity plotted is different from that in Fig. 5.

As argued above, if the surface is repeatedly scanned, this kind of dependence will lead to a diffusion coefficient that is proportional to T. Interestingly, the slope of the straight line is virtually independent of the emission rate Γ and the Rabi frequency Ω, provided that both are high enough to ensure that the molecule emits at least one photon during the time $t_{\text{probe}}=T/N$ when probed by the laser. This result is somewhat unexpected because photon emission is a source of dephasing and one expects dephasing to change the molecule's dynamics considerably. The insensitivity of the result to the parameters of the electromagnetic field suggests that the molecule stays effectively uncoupled from the laser most of the time except during the times the probe is near the molecule and a burst of photons is being emitted.

As known from the theory of quantum diffusion [28–30], dephasing and relaxation processes destroy the coherent transport and lead to a more classical-like behavior where $\langle(n-n_0)^2\rangle^{1/2}\propto T^{1/2}$. The failure of the dephasing caused by the interaction with the vacuum electromagnetic field, to destroy the coherent transport shows that scanning microscopy can be sufficiently nonintrusive to preserve quantum coherence. Loosely speaking, our finding is that ''while not seen, the molecule does not decohere.''

The situation changes when the pure dephasing rate γ is nonzero. Photoemission is no longer the sole source of dephasing. If the decoherence time $1/\gamma$ is shorter than T then coherent transport will be destroyed. Repeating the simulation for this case we find the behavior shown in Fig. 6. The mean square distance the molecule travels during the time between the bursts of photons is now closer to the relationship

$$\langle(n-n_0)^2\rangle\propto T$$

found in a classical diffusion process. Therefore if scanned repeatedly, the molecule will be found to undergo a diffusion process, with a diffusion coefficient that is independent of T. Relaxation processes, which also cause decoherence, similarly destroy the nonclassical behavior.

We conclude that the nonclassical behavior with a diffusion coefficient dependent on the scanning rate can be observed only if the molecule's decoherence time is longer than the time T it takes to scan the surface. Such a condition is not easy to meet experimentally. One possible experimental arrangement where such nonclassical measurement effects can be seen is with a laser cooled atom in a periodic optical lattice [11,34–39]. Unlike diffusion in solids, optical lattices exhibit extremely long coherence times that are limited only by residual scattering [35,36] and so it may be possible to satisfy the above stringent condition required to observe ballistic transport of a single atom.

We also note that our case of nonclassical diffusion is similar to the measurement induced diffusion described in Ref. [22] except that we deal with diffusion in real rather than momentum space. Similarly to the model described there, in our case repeated measurements result in a random diffusional motion of the molecule; the properties of this motion (the diffusion coefficient) depend on how frequently the measurement is performed (i.e., on the time T).

V. DOES DIFFUSION MAKE THE MOLECULE MORE "VISIBLE"?

Imagine for a moment that our molecule is glued to the surface. The average number of photons ν emitted by the molecule in a single scan (i.e., during the time T) is obviously proportional to the time t_{probe} the probe spends near the molecule and depends on the emission rate Γ and the intensity of the laser. Assuming that these three parameters remain fixed, how will ν change if the molecule is allowed to move? This issue is of practical interest because analytical chemists are often interested in the detection of minuscule amounts of chemicals in some small volume. Therefore given the limited photodetection efficiency, it is of interest to know how the signal depends on the molecule's mobility [13,15].

The net effect of the molecule's mobility on the emission signal is a tradeoff of two opposite trends. On one hand, the molecule can make a transition to another well during the time t_{probe} the probe samples the well. This shortens the time the molecule interacts with the probe and reduces the number of emitted photons. On the other hand, the probe may encounter the same molecule more than once thereby increasing the total number of photons. A simulation is required to resolve which of the two trends will dominate.

The quantum case is further complicated by the presence of coherences. Although we have performed fully quantum Monte Carlo wave function simulations, here we will limit the discussion to a somewhat simpler classical model, which can be obtained from the quantum model in the limit of large dephasing rate γ. In the classical model, the molecule performs diffusion, with a diffusion coefficient that can generally be different in the ground and excited electronic states. If the molecule is in the ground state, it can jump to the well on the right or left during a time dt, with probabilities each equal to $k_g\,dt$, where k_g is the rate constant for the jumps. Similarly, the excited molecule undergoes jumps with a rate constant k_e. If $k_e=k_g$ then photoexcitation does not affect the mobility of the molecule. If $k_e>k_g$ then photoexcitation increases the mobility.

We will also treat photoexcitation classically, assuming that it can be characterized by an excitation rate constant

$k_{ex}(I)$ that depends on the light intensity I. This implies that the light is incoherent.

Let $p_{n,g}$ be the probability that the molecule is located in well number n and is not excited and $p_{n,e}$ the probability to find an excited molecule in the nth well. The time dependence of these quantities is given by the equations

$$dp_{n,g}/dt = -2k_g p_{n,g} + k_g p_{n-1,g} + k_g p_{n+1,g} - k_{ex}\delta_{n,X(t)} p_{n,g} + \Gamma p_{n,e},$$

$$dp_{n,e}/dt = -2k_e p_{n,e} + k_e p_{n-1,e} + k_e p_{n+1,e} + k_{ex}\delta_{n,X(t)} p_{n,g} - \Gamma p_{n,e}. \quad (9)$$

Here $\delta_{n,X(t)}$ is equal to 1 if the position of the probe $X(t)$ is equal to n and 0 otherwise. The first three terms in each of the equations (9) describe surface diffusion, the last two terms, excitation by the probe and emission.

We study the dynamics of a single molecule governed by Eq. (9) by performing kinetic Monte Carlo simulations. We initially place our molecule in well number n where n is a random number from 1 to N. The molecule is initially in the ground state. After a short time interval dt, the molecule can jump to the left (n is decreased by 1), to the right (n is increased by 1), or get excited. The probabilities of these events are, respectively, $k_g dt$, $k_g dt$, and $k_{ex}\delta_{n,X(t)}dt$. When the molecule is in the excited state, it can emit a photon and go to the electronically ground state with a probability equal to $\Gamma\, dt$, or jump to the left or to the right. The Monte Carlo simulation is performed from $t=0$ to $t=T$.

Two cases are possible. We may assume that n is only allowed to take values from 1 to N. In this case a molecule that reaches the edge of the scanned area ($n=1$ or N) should remain within the scanned area. We achieve this by adopting periodic boundary conditions (if $n<1$ then set $n\rightarrow n+N$, if $n>N$ then $n\rightarrow n-N$). One can visualize this situation as a motion on the surface of a cylinder. Another possibility is that the molecule is allowed to travel outside the scanned area. It can leave it but it can also reenter it. In this case the well number n is unrestricted. Both situations can take place experimentally so we will study each of them.

A. $k_e = k_g$

In this case the molecule's mobility is unaffected by light. First let us estimate the number of photons ν_0 emitted during one scan by an immobilized molecule, $k_e = k_g = 0$. It is equal to the emission rate Γ times the average time τ_e the molecule spends in the excited state. The latter is equal to the time t_{probe} the molecule interacts with the probe times the probability p_e it is excited during that time. During the time t_{probe}, p_e and the probability $p_g = 1 - p_e$ that the molecule is not excited are related by $p_e\Gamma = (1-p_e)k_{ex}$, whence

$$\nu_0 = \Gamma t_{probe} p_e = t_{probe}/(\Gamma^{-1} + k_{ex}^{-1}). \quad (10)$$

If $\Gamma \gg k_{ex}$ then the number of photons is limited by the excitation rate, $\nu_0 = k_{ex} t_{probe}$ and if $\Gamma \ll k_{ex}$ it is limited by the emission rate, $\nu_0 = \Gamma t_{probe}$. If the molecule is now allowed to move, this effectively shortens the average duration of the period the molecule interacts with the probe so it is no longer equal to $t_{probe} = T/N$. However, the molecule can meet with the probe more than once during the scan. The resulting dependence of ν on the ratio k_e/Γ for the case $k_{ex} = 2\Gamma$ obtained from Monte Carlo simulations is presented in Fig. 7. In the case of the periodic boundary conditions ν monotonically increases with k_e. This is not surprising: as the molecule cannot leave the scanned area, it will encounter the probe more times as it becomes more mobile. However, when the scanned area is open and the molecule can leave it, ν exhibits a maximum as a function of the jump rate k_e. The number of photons emitted by the molecule will be the largest for a certain value of the molecule's mobility. A very rapidly or slowly diffusing molecule is less ''visible.''

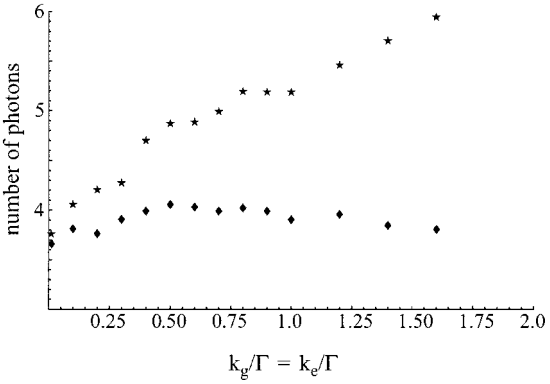

FIG. 7. The number of photons emitted by a molecule in a single scan as a function of k_e/Γ. The diffusion rate is the same in the ground and excited electronic states. Diamonds: the case of periodic boundary conditions. Stars: the molecule is allowed to leave the scanned area.

B. Photoinduced mobility case, $k_e > k_g$

If the molecule's diffusion is faster in the excited state than it is in the ground state, this leads to photoinduced diffusion. Photoinduced phenomena of this kind are often observed in single molecule spectroscopy [1,3,5,6]. Plotted in Fig. 8 is the number of photons ν as a function of k_e/Γ when k_g is kept constant and $k_{ex} = 2\Gamma$. The result is very different from case A: The number of photons emitted by the molecule in a single scan tends to decrease with increasing k_e, regardless of whether or not the molecule is allowed to leave the scanned area. This can be understood if we consider the limit where the diffusion coefficient in the ground state is zero and that in the excited state is very high. As soon as the laser excites the molecule that is located in well number n, it will jump to the well $n+1$ or $n-1$. Thus it is unlikely that the molecule will emit more than one photon from its original location because it is likely to move during the excitation-emission cycle. In other words, the molecule will emit only one photon every time it is encountered by the probe. However, it may be encountered by the probe more than once. Suppose the molecule jumped from n to n' when it was excited by the laser. Suppose also that the probe is moving in the direction with the increasing n. Since the molecule cannot move unless illuminated by light, if $n' < n$ then the probe

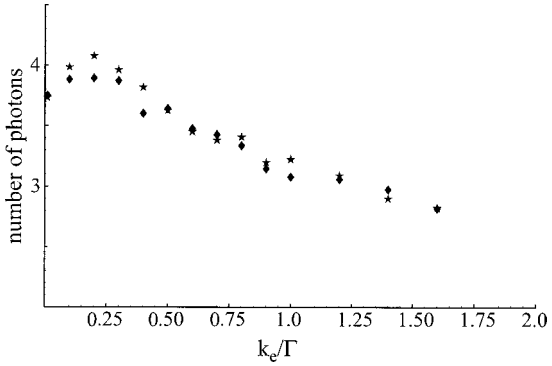

FIG. 8. The number of photons emitted by a molecule in a single scan as a function of k_e/Γ. The diffusion rate in the ground state is constant, $k_g/\Gamma=1$. Diamonds: the case of periodic boundary conditions. Stars: the molecule is allowed to leave the scanned area.

will never encounter the molecule again in the same scan. However, if $n'>n$ then the molecule will be illuminated again when the probe moves on to the n'th well. We see that the molecule will not be illuminated again with the probability $\frac{1}{2}$ and will emit a second photon with the probability $\frac{1}{2}$. Repeatedly applying this argument, to emit a total of $m+1$ photons, the molecule should jump to the right m times and then to the left. The probability of that is 2^{-m-1} so that the average number of additional photons the molecule will emit is

$$\langle m\rangle=\sum_{m=0}^{\infty} m2^{-m-1}=1. \tag{11}$$

Thus we expect that, in the limit of large k_e, ν should be close to $\langle m\rangle+1=2$, a result confirmed by the simulations. Since in the case of zero mobility, $k_e=0$, we estimated ν to be equal to $\nu_0=\tau/(\Gamma^{-1}+k_{\mathrm{ex}}{}^{-1})$, then we expect ν to be a decreasing function of k_e as long as $\nu_0>2$. We also note that our conclusion should not be affected much by the boundary conditions because the molecule cannot move much unless interacting with the probe and so it will not be likely to escape the scanned area. This is indeed confirmed by Fig. 8.

VI. SUMMARY AND DISCUSSION

Single molecule spectroscopy allows experimenters to follow the trajectories of individual molecules in time. If one tries to improve the spatial and temporal resolution of these methods eventually a limit is reached where the interaction of the molecule with the probe modifies the molecule's dynamics to the extent that it can actually be used to manipulate the molecule. Once this happens, a question arises about the meaning of the observed trajectories and about the amount of information on the molecule's dynamics that can be gained from such measurements. We have seen that a scanning probe can be a source of decoherence that changes the molecule's dynamics from coherent ballistic transport to a diffusional random walk. To observe this kind of effect other sources of decoherence must be sufficiently weak. We propose that this situation can be achieved for cold atoms in optical lattices.

Since the emission rate cannot be arbitrarily high, monitoring single molecule dynamics with a high temporal resolution requires good photodetection efficiency. If the molecule undergoes motion at a time scale comparable to that of emission then this motion affects properties of the emission process. The molecule can emit fewer or more photons depending on the relationship between its mobility and the emission rate. Photoinduced diffusion, however, tends to suppress the molecule's emission because it shortens the average time the molecule interacts with the probe.

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