Modifying atomic collision dynamics with intense ultrashort laser pulses

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It has been suggested that "short" pulses of intense laser radiation can modify atomic collision dynamics in new and interesting ways. Recent experimental results in sodium-argon vapor with 1.6-psec pulses verify the existence of such an effect, although smaller in magnitude and at somewhat higher field intensities than had been predicted from theoretical arguments. Using quantum-mechanical wave-packet propagation on a realistic potential-energy curve under the parameters of the experiment, we determine that the time between curve crossings, the standard against which pulse durations should be measured, is on the order of 0.8 psec or less. The experimental results can then be understood in the context of having used too long a pulse to have clearly observed short-pulse effects.

I. INTRODUCTION

The possibility of altering collision dynamics by the illumination of a collision system with laser radiation has been extensively investigated in recent years both theoretically[1–12] and experimentally.[13–22] Although the experiments are extremely difficult, as evidenced by the limited number of published observations, the possibility of selective control of the outcome of a collision event has given both chemists and physicists considerable motivation to pursue this line of investigation. Meanwhile, advances in the compression of optical pulses have led to the development of laser pulses of very short duration, in the femtosecond time domain. The duration of such a pulse is shorter than the collision time, so that the pulse irradiates only a portion of the collision event. (In contrast, a "long" nanosecond pulse not only illuminates the entire event but varies so slightly over the collision time as to be adequately described as a cw source.) Lee and George[9] suggested that significant effects might accompany such short-pulse irradiation of a collision system.

An explanation of the pulse-duration effect is quite straightforward: For a sufficiently short pulse it is possible that atoms can interact with the radiation as they approach and not as they rebound. In contrast, a long pulse will invariably interact with the system both times, with the distinct possibility that the second interaction will (at least partially) reverse the consequences of the first interaction. Specifically, consider the collision of two atoms in the presence of an applied radiation field of frequency ω. R_c is defined as the internuclear separation at which the potential-energy difference between the ground state and an excited state equals $\hbar\omega$; R_c is the location of the curve crossing between the dressed states. As the atoms collide, they pass through the point R_c twice, once on the inward journey, and again on the outward. If the pulse duration is long compared to ΔT_c, the time between these crossings, then the system is irradiated at both crossings. An excitation of the system might be induced at the first crossing, and since the interaction is still present, the system can be deexcited at the second. However, if the pulse duration is shorter than ΔT_c, the pulse might be present when the atoms pass through R_c on the inward path, but then the pulse would not be present as the atoms pass through R_c on the outward path, and so de-excitation could not be induced. (Of course, this situation is only one possibility—the pulse might not arrive at the precise time of the first curve crossing. An average over all possibilities must be performed to obtain a physically significant result.) Using the Landau-Zener formula, Lee and George predicted that such short pulses (i.e., pulses which are shorter in duration than the time between curve crossings) might be thousands of times more efficient in producing excited-state populations than a long pulse. Thus the duration of the pulse is a new parameter with which to investigate the modification of collision dynamics, and a critical one at that. (More recently, Lee and George[10] have investigated the shape of the pulse as well as its duration. They find much less dramatic differences between long and short pulses if the pulse is realistically smooth, rather than a square pulse, as used in their previous calculations.)

Following the Lee and George work, Sizer and Raymer[20] investigated the feasibility of observing pulse-duration effects in the sodium-argon system, using both a Landau-Zener model and a more rigorous Bloch-equation formalism. In these studies only straight-line, constant-velocity trajectories were investigated. Furthermore, the potential energy difference was modeled by a simple C_6/R^6 interaction, leading to the determination that $R_c = 6.0$ Å (≈ 11.3 bohrs). Given the temperature and laser detunings of their proposed experiment, the straight-line, constant-velocity trajectory yielded a typical time between curve crossings of 2.3 psec, leading them to conclude that a 1.6-sec pulse would be "short." Extensive semiclassical calculations were performed, indicating that an observable effect would be present, and so Sizer and Raymer proceeded to perform these very

difficult experiments and succeeded in observing an effect, albeit at significantly higher laser intensities than had been predicted. The purpose of the present work is to demonstrate that under the conditions of the experiment, and in light of realistic potential-energy curves, 1.6 psec cannot be considered a short pulse in the sense that we have described.

II. DESCRIPTION OF THE COLLISION DYNAMICS

In the previous theoretical investigations of Sizer and Raymer[20] and of Lee and George,[9–11] the effects of short-duration laser pulses on collision systems were studied using straight-line, constant-velocity classical trajectories. This method has proved valuable in a large number of investigations of atomic collision processes, particularly when the process is dominated by scattering at large impact parameters. However, the method is not valid at small impact parameters; in the limit of a zero impact parameter, the straight-line, constant-velocity approximation clearly fails. For the present problem, the relevant distances are on the order of 10 bohrs, something of an intermediate case with respect to the validity of the method. Under these conditions, the method would probably be sufficient to describe a conventional scattering process. However, the present problem is not conventional. In particular, the process depends in a crucial way upon ΔT_c, the time between curve crossings. This is a *dynamic* quantity, directly related to the forces exerted on the atoms during the collision, as derived from the potential. But the straight-line, constant-velocity-trajectory method makes no allowance for such forces—the potential may as well be constant. (The potentials entered the calculations of both Sizer and Raymer and of Lee and George by inducing transitions from one state to another, not by affecting the motion of the colliding atoms.)

More sophisticated semiclassical methods could be used to investigate this problem. Certainly, methods which utilize Hamilton's equations of motion to determine the classical trajectory would be more appropriate in this case than the straight-line, constant-velocity method. An alternative approach, which we adopt, is to treat the problem as rigorously as possible; since the dynamics are critically important to this process, let us use time-dependent quantum mechanics to propagate a wave packet describing the nuclear motion of the collision system. The question of "trajectory" is then easily addressed by calculating the expectation value of the wave packet's position as a function of time. Time-independent formulations are also possible, but an explicitly time-dependent formalism appears much more natural and intuitive, and hence preferable in building and securing an understanding of the basic physics. Furthermore, the major objection to time-dependent methods in general has been the lack of computationally tractable numerical methods—this objection has been largely overcome by the split-operator Fourier-transform method introduced by Fleck *et al.*,[21] so that time-dependent calculations are now feasible.

Interference phenomena are expected whenever there are two distinct paths to the same physical state. In the case of a long pulse, the two distinct paths correspond to photon absorption on the inward and outward legs of the collision event, while the same (final) state is an excited state of the collision system. Conversely, the interference is not present if only one path is available—this would occur if the second path were closed by virtue of the absence of laser irradiation. To determine the critical time between the first curve crossing and the second, and hence the availability of a second path leading to interference, we thus need only to consider motion in the ground electronic state. Ignoring spin-orbit interactions, this state is composed of two interacting S-state atoms and so the potential is isotropic and the total wave function for the nuclear motion having angular momentum l can be written as

$$\bar{\Psi}_l(\vec{r},t)=r^{-1}\psi_l(r,t)Y_{lm}(\theta,\phi)\ , \tag{1}$$

leading to the radial Schrödinger equation

$$i\hbar\frac{\partial\psi_l}{\partial t}=-\frac{\hbar^2}{2\mu}\frac{d^2\psi_l}{dr^2}+\left[V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right]\psi_l\ . \tag{2}$$

At time $t=0$ we specify that $\psi(r,0)$ is a wave packet localized at some point in the asymptotic region and moving toward the origin, and solve the time-dependent radial Schrödinger equation.

The split-operator Fourier-transform method is employed to propagate the wave function in time. A formal solution to the Schrödinger equation can be written in terms of the time evolution operator as

$$\psi(r,t+\delta_t)=e^{-iH\delta_t/\hbar}\psi(r,t)\ . \tag{3}$$

We then express H as $T'+V'$, where

$$T'=-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} \tag{4}$$

and

$$V'=V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\ . \tag{5}$$

Note that T' contains only derivative operators and V', the effective potential, only functions of the coordinate. Since T' and V' do not commute,

$$e^{-iH\delta_t/\hbar}\neq e^{-iT'\delta_t/\hbar}e^{-iV'\delta_t/\hbar}\ . \tag{6}$$

The Baker-Campbell-Hausdorff theorem states that

$$e^{\mathbf{A}}e^{\mathbf{B}}=e^{C} \tag{7}$$

if and only if

$$\mathbf{C}=\mathbf{A}+\mathbf{B}+(\mathbf{A},\mathbf{B})+\cdots\ . \tag{8}$$

We could approximate the evolution operator by Eq. (6), but a better approximation involves the symmetric decomposition of the evolution operator,

$$e^{-iH\delta_t/\hbar}\approx e^{-iT'\delta_t/2\hbar}e^{-iV'\delta_t/\hbar}e^{-iT'\delta_t/2\hbar}\ , \tag{9}$$

which has error of $O(\delta_t^3)$. The usefulness of this approximation rests on the ease with which the operator $e^{-iT'\delta_t/2\hbar}$ can be evaluated; fortunately, this is not

difficult using Fourier transforms. Denoting the Fourier transform of $f(r)$ by $g(k)$,

$$\mathcal{F}[f(r)]=g(k)\ , \tag{10}$$

the transform of the derivative is simply

$$\mathcal{F}\left[\frac{df}{dr}\right]=-ikg(k) \tag{11}$$

and

$$\mathcal{F}[e^{d^2/dr^2}f(x)]=e^{-k^2}g(k)\ . \tag{12}$$

The result of the exponential of the radial kinetic energy operator working on the wave function is then

$$e^{-iT'\delta_t/2\hbar}\psi(r,t)=\mathcal{F}^{-1}[e^{-i\hbar k^2\delta_t/4\mu}\mathcal{F}[\psi(r,t)]]\ . \tag{13}$$

The entire process of evolving the wave function in time reduces to a series of Fourier transforms, multiplications, inverse Fourier transforms, multiplications, etc. As the wave packet is propagated in time the expectation value of position is evaluated at each step and a quantum-mechanically-meaningful trajectory is obtained.

III. THE CALCULATION

To describe the intermolecular forces determining the motion of the colliding atoms, we employed the potential-energy curves of Saxon, Olson, and Liu.[22] For a detuning of 45 cm^{-1} on the low-frequency side of the sodium D_1 line, as used in the Sizer-Raymer experiments, R_c is found to be 9.4 bohrs. This is consistent with the 9.51 bohrs determined by Lee and George[11] using the experimentally derived curves of Tellinghuisen *et al.*[23] and of Goble and Winn,[24] although somewhat less than the 11.3 bohrs determined by Sizer and Raymer from the asymptotic limit of the potential.

The experiments were performed at 300°C, corresponding to a mean collision energy of 0.043 eV—the initial wave function was given a momentum k_0 consistent with this energy. (All our calculations were performed with this initial wave vector and do not include a thermal average.) The initial wave packet is given as

$$\psi(r,\,t=0)=[2\pi(\Delta r_0)^2]^{-1/4}\times\exp\left[-\frac{(r-\langle r\rangle_0)^2}{4(\Delta r_0)^2}+ik_0(r-\langle r\rangle_0)\right],$$

where Δr_0 represents the initial width of the wave packet and $\langle r\rangle_0$ its initial location; in these calculations, $\langle r\rangle_0=20$ bohrs. As the collision evolves, wave functions at subsequent times are calculated and $\langle r(t)\rangle$ determined. Examples of such calculations are exhibited in Fig. 1, which was obtained for an angular momenta $l=50\hbar$. The solid line represents $\langle r\rangle$ as a function of time for a wave packet with initial $\Delta r_0=0.5$ bohr. For the first picosecond the wave packet travels with nearly constant velocity. As it samples the potential at smaller separations, its velocity slows until $\langle r\rangle$ reaches its minimum value of 6.9 bohrs at $t\approx 1.5$ psec, at which time it rebounds and completes the collision event.

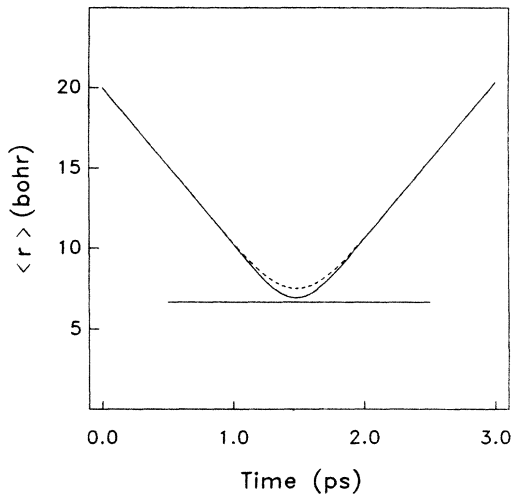

FIG. 1. Wave-packet position plotted as a function of time for the angular momentum $l=50\hbar$ for two different wave packets; the solid line indicates the quantum trajectory for a wave packet with $\langle r\rangle_0=0.5$ bohrs, while the dashed line is for a more delocalized wave packet with $\langle r\rangle_0=2.0$ bohrs. The classical turning point at 6.66 bohrs is indicated by the flat horizontal line.

Since the expectation value is a weighted average, the wave packet (as determined by $\langle r\rangle$) never reaches the classical turning point at 6.66 bohrs. (As the "leading" edge of the wave packet reaches the classical turning point, it is reflected and interferes with the remainder of the packet. After the wave packet has been reflected by the potential, the original shape of the wave packet is recovered.) A second curve, obtained from a wave packet with $\Delta r_0=2.0$ bohrs, is also exhibited in Fig. 1. Since

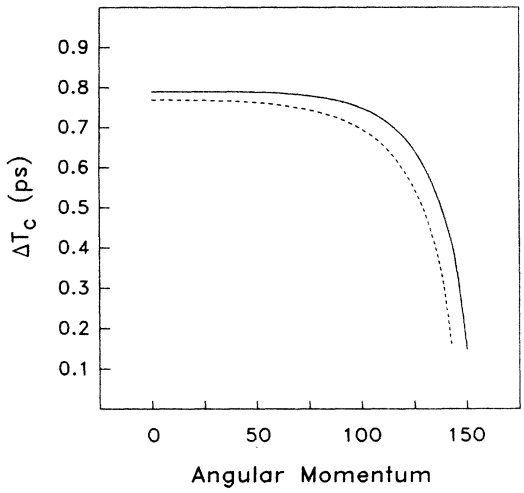

FIG. 2. Time between curve crossings, as determined by quantum-mechanical wave-packet propagation, plotted as a function of incident angular momentum. The solid and dashed lines refer to wave packets with $\langle r\rangle_0=0.5$ bohr and 2.0 bohrs, respectively, as in Fig. 1. For angular momenta greater than about $150\hbar$, the centripetal barrier is sufficiently high that the colliding atoms never reach the radiative interaction region.

the extent of the wave packet is greater, it experiences the potential earlier than the first wave packet, is slowed more quickly, and comes to rest at a larger internuclear separation. But it also rebounds more slowly, with the result that both wave packets take the same path in the asymptotic region.

From the trajectory information thus obtained, ΔT_c for a particular collision can be determined. From Fig. 1 we see that the more delocalized the wave packet, the smaller is the time between curve crossings. An upper limit on short is thus established by the more localized wave packets. The wave-packet propagation was repeated for various angular momenta, and the results presented in Fig. 2 were obtained. We see that the largest ΔT_c, associated with a "head-on" collision with zero angular momentum, is less than 0.8 psec and that ΔT_c decreases with increasing angular momentum. This functional dependence is very reasonable; as the angular momentum increases the classical turning point moves to larger internuclear separations so that the distance the atoms travel between curve crossings diminishes. Also, the difference between the localized and delocalized wave packets increases with increasing angular momentum. These calculations, which represent the conditions present in the Sizer-Raymer experiment, indicate that 1.6 psec cannot be considered a short pulse.

IV. CONCLUSIONS

Using quantum-mechanical wave-packet propagation techniques on realistic potential-energy curves, we have found that the time between curve crossings is never greater than 0.8 psec, providing an upper limit on what should be termed short. In contrast, the shortest pulse considered in the experiment was 1.6 psec. The implication is quite clear—the pulse used in the experiment was too long to clearly observe the effect of an ultrashort pulse.

Sizer and Raymer did observe an effect, although at substantially greater intensities than their own theoretical analysis, or the earlier one by Lee and George, had predicted. Sizer and Raymer argue that several factors, notably the spatial and temporal averaging inherently performed in a cell experiment, mitigate against them in this experiment. These factors were undoubtedly present, but our results clearly indicate that a shorter pulse should have been used to clearly observe short-pulse-duration effects. With such a short pulse, the field would be present at one curve crossing and absent at the other —we believe that what was actually observed in the experiment was the effect of different pulse intensities at the different curve crossings. That a pulse-duration effect was observable under these conditions suggests that for a sufficiently short pulse, the effect might indeed be dramatic.

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