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Wave-packet isotope separation using phase-locked pulses

J. R. R. Verlet, V. G. Stavros, and H. H. Fielding
Department of Chemistry, King's College London, Strand, London WC2R 2LS, United Kingdom

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We introduce a general wave-packet isotope-separation scheme exploiting the optical Ramsey method. Optically excited molecular wave packets in different isotopes develop a well-defined phase difference after just a few vibrational periods. Phase-locked pairs of optical pulses are able to selectively pump one isotope back down to the ground state and enhance the excited-state population of the other isotope. The method is illustrated by simulating wave-packet isotope separation of a mixture of $^{79}Br_2$, $^{81}Br_2$, and $^{79}Br^{81}Br$. We also exploit phase-locked pairs of optical pulses to reduce the time required for the spatial separation of wave packets.

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I. INTRODUCTION

A significant amount of research is currently aimed at studying the time-dependent behavior of wave packets with the goal of customizing them to control atoms and molecules. Several control schemes exist that use light to drive atoms or molecules along predetermined pathways, all of which exploit the coherence of laser light to manipulate the quantum-mechanical phase relationships between the various eigenstates of the system. The wave-packet approach to coherent control was first introduced by Tannor and Rice [1] and employs sequences of ultrashort light pulses whose frequencies, amplitudes, and phases are tailored to steer the wave packet into a predetermined state at a later time. In this paper we demonstrate how multiple wave-packet excitation can be exploited to separate mixtures of isotopes on time scales of just a few vibrational periods.

Conventional methods of isotope separation exploit the tiny differences in isotopic mass and involve centrifugation and gaseous diffusion [2]. Their main attraction is their large-scale capability but the drawback is that enrichment rates are very slow. An alternative approach is laser isotope separation, which is critically dependent on the tiny spectroscopic shifts of the isotopes and involves using tuneable narrow bandwidth lasers to selectively excite one specific isotope [3,4]. Recently, Averbukh *et al.* proposed and demonstrated laser isotope separation using wave-packet technology [5]. In their method, molecular wave-packets of different isotopes become spatially separated during the course of their long-time evolution due to the isotope dependence of the vibrational frequencies and anharmonicities. The principle is illustrated by considering a 1:1 mixture of $^{79}Br_2$:$^{81}Br_2$ [5]. A bandwidth limited 60-fs pulse excites ground-state molecules to the B state of Br_2 with average vibrational quantum number $v'=15$. Wave packets with $v'=15$ have vibrational periods $\tau_{79}=303$ and $\tau_{81}=310$ fs. These differences are imperceptible at short times, but eventually the wave packets in each isotope will become spatially separated. Owing to the anharmonicity of the molecular potentials the wave packets disperse, break up into smaller sub-wave-packets called partial revivals, and eventually reform at so-called revivals [6,7]. For efficient isotope enrichment the wave packets must be out of phase by 180° *and* well localized. In the Br_2 example, the first time that both these conditions are satisfied is around 32 ps. In Fig. 1(a) we present a schematic of the excitation scheme and in Fig. 1(b) a calculated recurrence spectrum illustrating the 4th revival around 32 ps where efficient isotope enrichment is possible. This region of the spectrum is expanded in Fig. 1(c).

In this paper we employ a coherent control approach to isotope separation, which exploits the phase differences between wave packets in different isotopes rather than just their long-time spatial separation. One advantage of this approach is that it allows the isotopes to be separated at much shorter time scales. The idea came from the phase-sensitive or phase-modulated detection technique, which was initially developed for monitoring vibrational wave-packet dynamics [8], and subsequently applied widely to electronic wave-packet detection [9]. It relies on the interference of a pair of identical phase-locked wave packets in the weak-field limit. Briefly, exciting a superposition of vibrational states from the ground state creates a pump wave packet, which evolves in the excited-state potential. When the pump wave packet returns to its initial coordinates a probe wave packet is created. By varying the phase difference between the two wave pack-

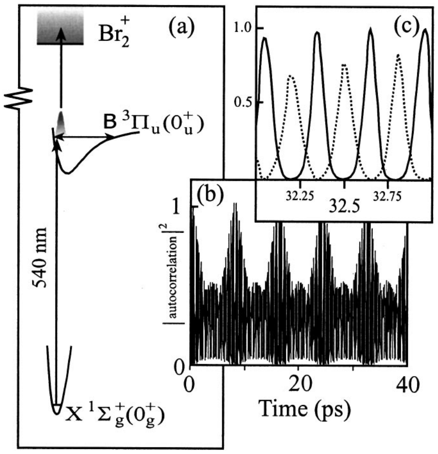

FIG. 1. (a) An outline of the excitation scheme employed in the Br_2 isotope separation methods described in this paper and also in the work of Averbukh *et al.* [5] and Leibscher and Averbukh [9]. A calculation illustrating the dispersion and revival structure of a vibrational wave packet with $v'=15$ in the B state of Br_2 (b) together with a close up of the region around 32 ps where the wave packets in the $^{79}Br_2$ and $^{81}Br_2$ isotopes are spatially separated [5] (c).

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ets it is possible to maximize the excited-state population of one isotope whilst minimizing that of the other. Leibscher and Averbukh recently observed quantum interference effects between wave-packets created in the same molecular potential in an optimal control scenario also aimed at isotope separation [10]. In their work they employed a linear optimization procedure to generate laser fields that result in a maximum difference between the ionization probabilities of two isotopes at a fixed time interval. When the interaction time of their laser pulse was longer than one vibrational period, the optimal field looked like a pair of two separate laser pulses with different shapes. The basic principle underlying our approach and the optimal control method of Leibscher and Averbukh is the same—quantum interference. However, our approach is more intuitive as it employs phase-locked pulse sequences rather than feedback-optimized exotic field shapes.

Let us give a physical picture of isotope separation using phase-locked pulse sequences. The time taken for a vibrational wave packet to move from one side of the well to the other and back again depends on the average frequency ω of the states supported by the potential and may be written as $T_{cl}=2\pi/\omega$. The molecular-mass dependence of this vibration period ensures that it takes a little longer for the heavier isotope to complete a full vibration. For a typical molecule, this time difference is just a few femtoseconds and only leads to spatial separation after numerous vibrations (Fig. 1). For optical excitation, this time difference can be interpreted in terms of an optical phase of the excitation pulse. The optical phase can be exploited by exciting the isotopes at carefully chosen wavelengths so that the optical phase of the wave packets in each isotope are an odd multiple of π, and, therefore, out of phase, after an integral number of vibrations. A second identical, phase-locked laser pulse will then enhance or deexcite the population in the excited state depending on the optical phase difference between the two pulses. Since the two isotopes are out of phase at the time the probe wave packet is launched, enhancing one isotope will inevitably pump the other isotope back to the ground state. Once separation is achieved in this manner, the desired isotope may be extracted by ionization with a third photon from this state.

II. THEORY

We illustrate the use of the above method by first simulating wave-packet isotope separation of a 1:1 mixture of $^{79}Br_2$ and $^{81}Br_2$ molecules and then a mixture of all three isotopes. A molecular isotope mixture is subjected to a pair of identical laser pulses with spectral profile $f(\omega)$ and forms a superposition state written as

$$\Psi(t)=\sum_j f(\omega)\langle j|\mu|i\rangle\{\exp(-i\omega t)+\exp[-i\omega(t+\Delta t+\phi)]\}, \quad (1)$$

where $|i\rangle$ is the initial state and $|j\rangle$ are the excited states. The first exponential term in curly brackets defines the temporal evolution of the first wave packet. The second exponential term represents a second wave packet excited after a time Δt. This second wave packet is the probe wave packet that drives the separation and is phase locked to the initial wave packet through a phase ϕ. We can conveniently monitor the evolution and probability density of this quantum state by measuring the autocorrelation of the wave packet $\langle\Psi(0)|\Psi(t)\rangle$. Molecular bromine is excited from its ground state $v''=0$ to a small number of vibrational states v' in the B state using optical pulses of around 540 nm. Accurate potentials were calculated using Leroy's program employing the RKR method [11] from accurate spectroscopic constants for the individual isotopes in the mixture [12]. These potentials were then used to calculate vibrational energies and wave functions by numerically integrating the Schödinger equation using the Numerov-Cooley method [13] with the program of LeRoy [14].

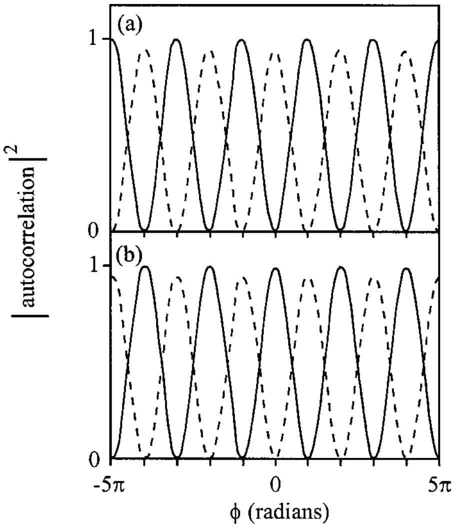

FIG. 2. Excited-state populations of the $^{79}Br_2$ (solid lines) and $^{81}Br_2$ (dashed lines) as a function of the phase difference between the excitation pulses. In (a) the probe wave packet is created after 2 $^{81}T_v$ maximizing the population of the $^{81}Br_2$ isotope when $\phi=n\pi$ with n zero or even, and maximizing the population of the $^{79}Br_2$ isotope when $\phi=n\pi$ with n odd. In (b) the probe wave-packet is created after 2 $^{79}T_v$, shifting the population maxima by π.

III. RESULTS AND DISCUSSION

Unfortunately, an optical phase of π between the wave packets in the different isotopes cannot be achieved after just one vibrational period of the wave packet for excitation to the B state, but it is possible after two oscillations. An 80-fs transform-limited Gaussian pulse excites a wave packet centered around $v'=21.5$. The vibrational period T_v of this wave packet is approximately 400 fs. At this energy, the difference in the vibrational period for the two isotopes is around 4 fs, corresponding to $9\pi/2$ at this particular wavelength. After two oscillations, at a time $t=2T_v+\phi$, the wave packets in each isotope will be out of phase with one another and the probe wave packet is launched. Figure 2 illustrates the effect of varying the phase ϕ, on the population of each isotope in the excited electronic state of the separation. When the probe wave packet is launched at twice the period of the

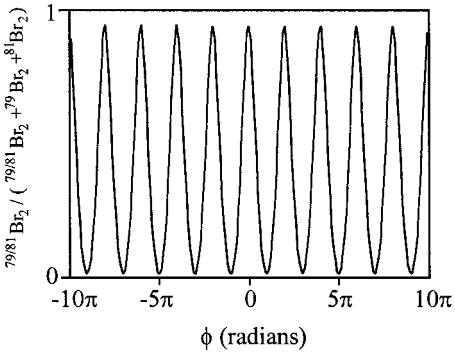

FIG. 3. The population of the mixed isotope as a fraction of the total excited-state population of all three isotopes, following excitation by a pair of pulses separated by 4 $^{79,81}T_v+\phi$.

$^{81}Br_2$ isotope 2 $^{81}T_v$ [Fig. 2(a)], for $\phi=0$, the population of the $^{81}Br_2$ isotope is at a maximum whereas the population of the $^{79}Br_2$ isotope is zero. This is expected as the wave packet in the $^{79}Br_2$ isotope is exactly out of phase with that in the $^{81}Br_2$ isotope. As the phase is scanned, the $^{81}Br_2$ population is a maximum whenever $\phi=n\pi$ and n is even whereas the $^{79}Br_2$ population is a maximum whenever $\phi=n\pi$ and n is odd. Similarly, when the probe wave packet is launched at 2 $^{79}T_v$ [Fig. 2(b)], the population of the $^{79}Br_2$ isotope is maximum at $\phi=n\pi$ when n is zero or even and the population of the the $^{81}Br_2$ isotope is maximum at $\phi=n\pi$ when n is odd. The efficiency of separation is limited by the dispersion of the wave packet. By ensuring that only a small number of states are excited in the superposition so that the local energy spacing approximates better to a harmonic potential, spreading of the wave packet is minimized and the wave packets more or less retain their original shape during the first few vibrations. The efficiency of the separation illustrated in our calculations is virtually unity. There will of course be some molecular systems for which separation will be possible after just one vibrational period making the technique more efficient.

More realistically, molecular bromine exists as a mixture of the three isotopes $^{79}Br_2$, $^{79}Br\,^{81}Br$ and $^{81}Br_2$ in a 1:2:1 ratio. The cross isotope may be separated from the other two in a similar fashion. As the reduced mass of this isotope lies approximately in the middle of the reduced masses of $^{79}Br_2$ and $^{81}Br_2$, after one vibration the optical phase relationship between a wave packet in the cross isotope and wave packets in the other two is $\sim\pm\pi/4$. At the fourth return of the three wave packets to the Frank-Condon region, $^{79}Br_2$ and $^{81}Br_2$ will be in phase with one another but the wave packet in the $^{79}Br\,^{81}Br$ isotope will be out of phase with the other two. Despite increased dispersion after four vibrations with an 80-fs pulse, the $^{79}Br\,^{81}Br$ isotope may still be separated with a very high efficiency as shown in Fig. 3. The population of the mixed isotope is plotted as a fraction of the total excited-state population of all three isotopes, following excitation by a pair of pulses separated by 4 $^{79,81}T_v+\phi$. The population of the $^{79}Br\,^{81}Br$ isotope is maximized and the populations of the $^{81}Br_2$ and $^{79}Br_2$ iotopes are minimized when $\phi=n\pi$ with n zero or even.

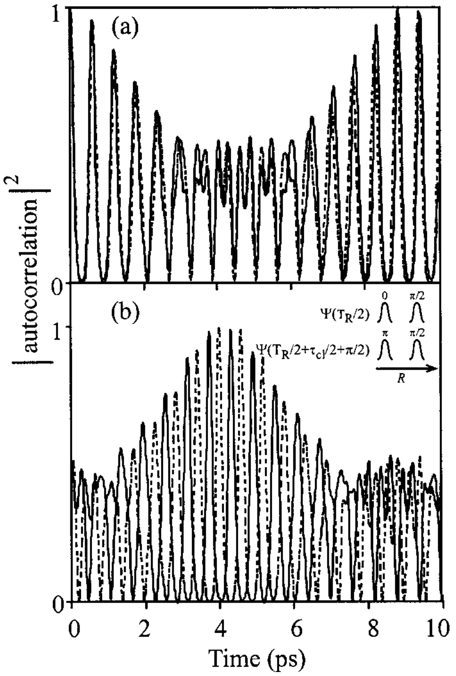

FIG. 4. (a) A calculation illustrating the dispersion and first revival of a mixture of $^{79}Br_2$ (solid) and $^{81}Br_2$ (dashed) isotopes following excitation around $v'=29$ with a 125-fs bandwidth limited Gaussian pulse. At this energy the two isotopes will be spatially separated at the 3rd full revival. (b) A calculation illustrating the shift of the revival structure following excitation by a pair of phase-locked pulses separated by $1.5T_v+\pi/2$. The inset is a cartoon to illustrate how the little wave packets interfere at the 2nd-order partial revival. The upper picture shows the first wave packet split into two components, one at each end of the internuclear coordinate. These "little" wave packets have a phase difference of $\pi/2$ between them [6]. The lower picture shows the second wave packet which has evolved an additional $T_v/2$ (having the effect of flipping the two phases round) and has an additional phase of $\pi/2$. The result is that the "little" wave packets at the inner turning point interfere destructively while those at the outer turning point interfere constructively, turning the partial revival pattern into a full revival pattern.

Continuing with the theme of phase-locked pairs of pulses it is worth pointing out that phase-locked pairs of pulses can also be exploited to improve the time scale of spatial separation. Let us give a physical picture of such a scheme. If we excite pairs of phase-locked wave packets at odd half-integral values of the vibrational period, the second wave packet will be created when the first wave packet is at the outer turning point. Interference between the two wave packets is not possible since they do not overlap spatially. The pair of wave packets will evolve independently until they are delocalized across the vibrational coordinate. The delocalized wave packets are able to interfere and the resulting interference pattern is controlled by the phase difference introduced at $t=0$. Around the time of the second-order partial revival, each wave packet has split into a pair of partially revived "little" wave packets, which are themselves separated by half a vibrational period. The phase difference between each of the "little" wave packets is $\pi/2$ [6]. The original wave packets were separated by half a vibrational period and so the phases of the "little" wave packets originating from one excitation pulse will be reversed with respect to those originating from the other. If, for example, the phase difference between the initial wave packets is $+\pi/2$ or $-\pi/2$, the ‘‘little’’ wave packets located at the inner turning point will have a phase difference of either π (destructive interference) or 0 (constructive interference) and those at the outer turning point will have a phase difference of 0 or π, respectively—the net result is a *single* wave packet localized at either the outer or inner turning point. Thus, instead of seeing peaks in the recurrence spectrum at twice the vibration frequency (a second-order partial revival) peaks are observed at the vibration frequency (a full revival). In fact, the whole pattern of partial and full revivals is shifted by half a revival. Exploiting this shift in the interference pattern allows us to reduce the time required to separate isotopes spatially.

The technique is illustrated in Fig. 4. Excitation around $v'=29$ with a 125-fs bandwidth-limited Gaussian pulse, generates a vibrational wave packet with an approximate vibrational period of $T_v=600$ fs. Around the time of the first full revival (9 ps) it is barely possible to separate the two isotopes [Fig. 4(a)] and in fact it would be necessary to wait until the 3rd revival to observe complete spatial separation. However, excitation by a pair of phase-locked pulses separated by 1.5 $^{79}T_v+\pi/2$ shifts the pattern of revivals and partial revivals so that the isotopes are more or less spatially separated after approximately 4 ps as illustrated in Fig. 4(b). Unfortunately complete spatial separation is not quite achieved because the two isotopes are already slightly separated at the first revival. This cannot be compensated for by changing the excitation energy because the π phase difference will be lost.

IV. SUMMARY

We have demonstrated that it is possible to employ phase-locked pairs of optical pulses to separate mixtures of two or three isotopes. Our method of wave-packet isotope separation has some advantages over others. First of all, the wave packets need not be separated spatially at either end of the potential. Instead, separation occurs after just one or two vibrations, i.e., <1 ps. Second, as this is an interference technique, it is possible to achieve *complete* isotopic separation which is in contrast with the spatial separation technique in which the bandwidth associated with the wave packet prevents the two isotopes being entirely separate since their wave-packets overlap at the edges. Third, because the separation is induced after only a few periods, the method is also applicable to a large number of polyatomic molecules, whose decay routes are much more rapid. One limitation of the method is that one must choose a system in which it is possible to excite with a wavelength where there is a π phase difference between the wave packets in the two isotopes after just a few vibrational periods. The fewer vibrational periods one has to wait the less dispersion and the better the isotope separation. One obvious disadvantage of the method is that it relies on working in the weak-field limit, although Chen and Yeazell have suggested that interference techniques can be employed in strongly driven electron wave-packet systems [15]. We have also illustrated that it is possible to improve the time scale of isotope separation based on spatially separated wave packets, by exploiting phase-locked pairs of pulses instead of a single short laser pulse. It is worth noting that Leibscher and Averbukh have illustrated that pulse-shaping techniques exploiting the interference and spatial separation of wave packets can also be employed to separate isotopes [10]; however, we believe that our approach of phase-locked optical pulses is more intuitive and that it is probably less experimentally challenging.

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