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Wave Packet Isotope Separation

I. Sh. Averbukh
Department of Chemical Physics, Weizmann Institute of Science, Rehovot, 76100 Israel

Marc J. J. Vrakking,* D. M. Villeneuve, and Albert Stolow
Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario Canada K1A 0R6

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We introduce and demonstrate a general wave packet method for laser isotope separation. In this scheme, laser excited molecular (or atomic) wave packets of differing isotopes become *spatially* separated in the course of their long-time free evolution. In order to overcome the quantum spreading of wave packets, we make use of the phenomenon of revivals. We demonstrate experimentally, with mixed $^{79}Br_2/^{81}Br_2$ isotopes, that significant control over the isotope ratio can be achieved in a single shot. [S0031-9007(96)01386-5]

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Wave packets are coherent sums of quantum states created by short, phase-controlled optical pulses. Wave packets exhibit spatial localization and, hence, as objects belonging to both the classical and quantum worlds, are useful for investigating fundamental aspects of quantum mechanics, such as the correspondence principle limit [1]. The free evolution of wave packets is directly related to the dynamics of the system and, consequently, wave packet methods are used to study fast processes in atomic [1], molecular [2], and condensed matter [3] physics. We suggest that wave packet techniques and methods of analysis should be considered together as a general and flexible "technology" to be applied to a variety of practical problems. In this Letter, we introduce and demonstrate the laser separation of isotopes based upon the preparation (and subsequent "extraction") of spatially localized wave packets, as one example of this novel technology.

Traditional methods of isotope separation such as gaseous diffusion and centrifugation rely on slight differences in isotopic mass [4]. Laser isotope separation [5], on the other hand, relies on small isotope shifts [6] in atomic or molecular spectral lines. It requires both the use of tunable narrowband radiation for selective excitation of one isotope over the others and a detailed knowledge of the spectroscopy of the system. Another approach to the laser separation of specific odd-mass atomic isotopes combined high resolution selection with Zeeman and hyperfine quantum beats [7]. We introduce here wave packet isotope separation [8] which, by contrast, does *not* rely on spectrally selective excitation. Rather, it makes use of differences between isotopes in terms of the *free* evolution of wave packets. For the case of excitation of vibrational wave packets (the example we use to illustrate the method), the isotopes become separable due to differences in the wave packet evolution arising from the isotope dependence of vibrational frequencies and anharmonicities. At the point of optimal spatial separation of the wave packets, one isotope may be selectively extracted (e.g., by ionization) through use of another laser pulse. Wave packets, however, delocalize (spread) as they evolve. In order to overcome this quantum spreading, we take advantage of the wave packet phenomena known as revivals [9] and fractional revivals [10], as discussed below.

Wave packet isotope separation combines the advantages of mechanical separation schemes (generality, robustness) with the high single-step enrichment typical of laser separation schemes. The "separation machine" operates at the single molecule level and, because it relies only on the internal dynamics, it is inherently Doppler free.

In order to illustrate the method, we consider the simple case of a two-component (α and β) isotope mixture of diatomic molecules. We assume that the molecules are initially in the zeroth vibrational state of the ground molecular potential, $V_0(R)$. A short laser pulse $E_1(t)$ of central frequency ω_1 excites the molecules to a higher bound molecular potential, $V_1(R)$. The duration of the excitation pulse is much shorter than the vibrational periods, T_α and T_β, of both isotopes in the $V_1(R)$ potential, where $T_{\alpha,\beta} = 2\pi/\omega_{\alpha,\beta}$ (and $\omega_{\alpha,\beta}$ are the vibrational frequencies). The isotope shift is defined as $\Delta\omega = |\omega_\alpha - \omega_\beta| \ll \omega_{\alpha,\beta}$. For each isotope, a spatially localized vibrational wave packet is prepared in the upper electronic state by the excitation pulse. It should be stressed that no *spectral* selectivity is used at this stage and virtually identical wave packets are excited for both isotopic components.

The wave packets initially undergo periodic oscillatory motion in the V_1 potential. If the vibrational wave packets in the molecules α and β behaved exactly like classical particles, they would become spatially separated after a time period $t_{\mathrm{sep}} \approx \pi/\Delta\omega$, since at this time the classical vibrational motions of the two wave packets would be exactly 180° out of phase. However, quantum mechanical dephasing caused by anharmonicity in the molecular potentials leads to a delocalization of the wave packets [10] after a time $t_{\mathrm{deph}} \approx T_{\mathrm{rev}}/(\Delta n)^2$. Here Δn represents the typical number of vibrational states contained in the wave packet. The quantity Δn is determined by the bandwidth of the excitation pulse and properties of the absorption band. The revival time $T_{\rm rev}$ is defined as [10]

$$T_{\rm rev} = \frac{4\pi}{\omega(E)} \left| \frac{d[h\omega(E)]}{dE} \right|^{-1}, \tag{1}$$

where $\omega(E)$ is the oscillation frequency in the V_1 potential of a classical particle with energy E. As an example, for the case of a Morse oscillator with energy $E(v) = h\omega(v - \kappa v^2)$ and vibrational quantum number v, frequency ω, anharmonicity κ, the revival time is $T_{\rm rev} = 2\pi/\omega\kappa$. We note that the time scale $T_{\rm rev}$ is much longer than both the vibrational periods $T_{\alpha,\beta}$ and the dephasing time $t_{\rm deph}$.

After a time $t \approx t_{\rm deph}$, the wave packets of both isotopes are completely delocalized over the classically allowed region. The simple classical-like idea for spatial separation of isotopic wave packets fails for $t_{\rm deph} \leq t_{\rm sep}$. The solution to this problem comes from the phenomenon of revivals. As the wave packets under consideration consist of a finite number of discrete states, they almost completely restore their initial form in the course of time. It was shown [10] that groups of strongly localized wave packets appear around times $t \approx (m/n)T_{\rm rev}$, where m/n is an irreducible fraction of integers. For example, around time $t \approx \frac{1}{2}T_{\rm rev}$, the half revival, the first recurrence of the wave packet to its original shape takes place. The effects of dephasing only manifest themselves in a 180° phase shift of the wave packet motion with respect to the initial motion. Around time $t \approx T_{\rm rev}$, the full revival, the wave packet revives without any phase shift and appears exactly as the initial wave packet. For $n > 2$, fractional revivals of the original wave packet occur where the wave packet splits into a number of smaller sub-wave-packets. We note that revivals and fractional revivals of wave packets have been observed both in atomic [11–14] and molecular systems [15–18].

The Franck-Condon principle states that molecular electronic transition probabilities are related to nuclear radial overlap integrals (Franck-Condon factors). The transition is vertical and spatially localized near the stationary phase points (called Condon points) of these overlap integrals. The spatial selectivity of the probe step in vibrational wave packet experiments is due to this phenomenon. Therefore, at the time of optimal isotope separation, an extraction laser pulse $E_2(t)$ with central frequency ω_2 may be applied which further excites only one of the isotopes, say, β, to an ionic molecular potential $V_2(R)$. The other isotopic component α remains in the potential $V_1(R)$ because it has an unfavorable geometry for excitation by the extraction laser pulse $E_2(t)$. The extraction of component α at this time delay would require a different laser pulse with central frequency ω_3. Thus the free evolution of the wave packet has effectively transformed a small isotopic shift into a large detuning of the electronic transition.

We illustrate the method by considering isotope separation of a mixture of ^{79}Br$_2$, ^{81}Br$_2$ isotopes. In Fig. 1, calculated autocorrelation functions are shown for vibrational wave packets in the electronic B state prepared by Gaussian laser pulses with a duration of about 60 fs. The central frequency of the preparation pulse was chosen such that a set of vibrational levels around $v' = 15$ was excited. In the initial stage of the wave packet evolution a sequence of peaks are seen [see Fig. 1(a)] which reflect the classical oscillation of the wave packets with a period of about 300 fs. Based on the anharmonicity, the calculated revival time of this group of levels is $T_{\rm rev} \approx 16$ ps. This revival structure can be seen in Fig. 1(b), which presents an overview of the autocorrelation function on a long time scale. In Fig. 1(a), the beginning of the separation of heavy and light isotopes can already be seen, but the wave packets delocalize before full separation occurs (i.e., $t_{\rm deph} \ll t_{\rm sep}$). In Fig. 1(c), we see that near one of the revival times (near $t \approx 32$ ps, i.e., $t \approx 2T_{\rm rev}$) the oscillations in the autocorrelation functions for the ^{79}Br$_2$ and ^{81}Br$_2$ isotopes occur out of phase, indicating a complete spatial separation of the isotopes.

The best isotope separation is expected at times when

$$t \approx jT_{\rm rev}(E)/2 \approx (2k + 1)\pi/\Delta\omega(E), \tag{2}$$

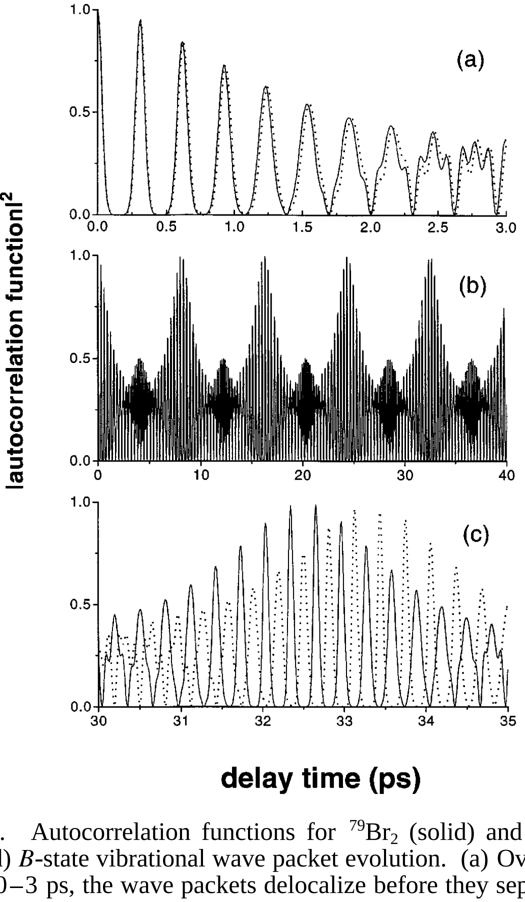

FIG. 1. Autocorrelation functions for ^{79}Br$_2$ (solid) and ^{81}Br$_2$ (dotted) B-state vibrational wave packet evolution. (a) Over the range 0–3 ps, the wave packets delocalize before they separate. (b) ^{79}Br$_2$ wave packet evolution over the range 0–40 ps, showing revivals and fractional revivals. The ^{81}Br$_2$ appears similar on this scale and is omitted for clarity. (c) Within the range 30–35 ps, one of the full revivals occurs. Furthermore, in this range the wave packets are simultaneously localized and spatially separated, allowing for isotope separation.

where j, k are integers. The first part of the equation ensures that the wave packets are well localized. The second part requires the wave packet oscillations of the two isotopes to be out of phase by 180°. Thus Eq. (2) provides *both* a value for the required central energy E of the wave packet and the field-free evolution time required for separation. The only quantity required to determine the optimal parameters is $\omega(E)$, which may be determined either from the molecular potential or directly from experimentally measured spectra.

To clarify the concepts introduced above, we present a contour map, shown in Fig. 2, which gives the time dependence of the *spatial overlap* integral between two isotopic wave packets, as a function of the central excitation frequency and the pump-probe time delay. At the initial stage of evolution, where the localized wave packets start together and move in phase, this overlap function is close to unity. As time goes on, the overlap quickly becomes much smaller, but is periodically restored at times $t \approx 2kt_{\text{sep}}$. The family of "vertical" lines with arrows in Fig. 2 are the lines of minimal overlap, labeled $k = 0, 1$ as discussed above in Eq. (2). On the same plot, a family of "horizontal" lines showing the dependence of the revival times on the central frequency of the preparation pulse are shown and labeled $j = 1, 2, 3, 4$ as discussed above in Eq. (2). In the regions near the intersections of the j and k lines, the isotopic wave packets have *both* spatial localization (i.e., a revival) and the smallest possible overlap (i.e., 180° shift): these are the regions where the best isotope separation can be achieved. In the experimental demonstration of wave packet isotope separation, discussed below, we chose the case ($k = 0, j = 4$) as emphasized by the circle around that point in Fig. 2.

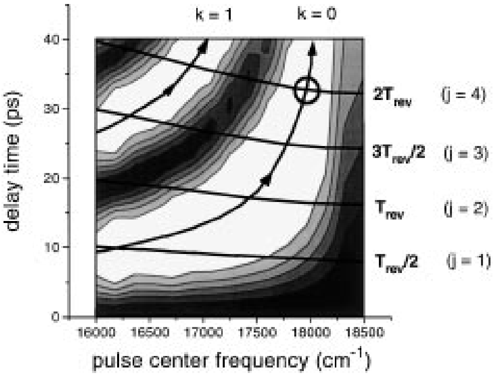

FIG. 2. Contour plot of the spatial overlap of $^{79}Br_2$ and $^{81}Br_2$ isotopic wave packets, shown as a function of time and the excitation pulse central frequency. The horizontal lines indicate the combinations of central frequencies and time delays at which the wave packet revives. They are labeled $j = 1-4$. The vertical lines indicate the times of minimum overlap of the isotopic wave packets and are labeled $k = 0, 1$. The points of intersection (j, k) are the points where the wave packets are *simultaneously* localized and spatially separated—the points of optimal isotope separation. The circle indicates the point $(j = 4, k = 0)$ where the experiments were performed.

The experimental apparatus used for wave packet isotope separation has been described in detail elsewhere [17,19]. Briefly, a synchronized femtosecond Ti:Sa and picosecond Nd:YAG laser system [20] was used to create femtosecond pump and probe pulses. The pump preparation pulse (variable between < 80 and 120 fs) was tunable between 547 and 590 nm and was used to prepare wave packets on the B states of the isotopically mixed Br_2 molecules. The probe extraction pulse (80–100 fs) was fixed at 340 nm and was used to ionize the B-state wave packets through a nonresonant two-photon step. A computer-controlled stepping motor varied the time delays between the pump and probe pulses (0–50 ps). A pulsed jet (1% in He) introduced cold Br_2 into the interaction region of a molecular beam photoelectron-photoion mass spectrometer. The time-of-flight mass resolution allowed for simultaneous monitoring of the $^{79}Br_2{}^+$ and $^{81}Br_2{}^+$ ion signals. Care was taken to ensure that the measured signals were not saturated with respect to the pump or probe steps (i.e., no higher order effects).

In Fig. 3(b) we present the measured $^{79}Br_2{}^+$ and $^{81}Br_2{}^+$ signals as a function of delay between pump and probe pulses. A number of revivals can be seen. In Fig. 3(a), the ratio of the isotopes (the measure of separation) is shown over the time domain 0–2.5 ps. It can be seen that due to the spatial overlap and the spreading of the wave packets, the separation is poor. The ratio of the isotopes is shown, in Fig. 3(c), for the time region around the point ($k = 0$, $j = 4$) which is encircled in Fig. 2. This point also corresponds to the situation shown in Fig. 1(c) ($t \approx 32$ ps $\approx 2T_{\text{rev}}$). Deep modulations in the isotope ratio can be seen, demonstrating the success of the wave packet isotope separation scheme. By simply changing the extraction pulse delay time, the single-shot isotope ratio can be varied by about 250%.

In conclusion, the optimal times for wave packet isotope separation were shown to be those for which the isotopic wave packets were out of phase concomitant with a full revival. The selectivity of the above separation scheme might be dramatically increased by making use of the interference of several evolving wave packets (produced by multiple pump pulses) [8] or by excitation of superlocalized squeezed wave packets [21]. In order to be of practical interest, stronger pump pulses may be used for excitation of larger fractions of molecules. This introduces Rabi oscillation, Stark shifting, etc., which will alter phases and amplitudes within the wave packet but still prepare a well-localized state. As the scheme presented here relies on *field-free* wave packet evolution, the essential physics of the isotope separation remains the same in this strong pump case. Wave packet isotope separation may also be applied to the separation of atomic isotopes, through the use of radially localized [22,23] Rydberg electronic wave packets. The present work provides an example of "wavepacket technology," as applied to the problem of laser isotope separation. We can foresee other applications, and we

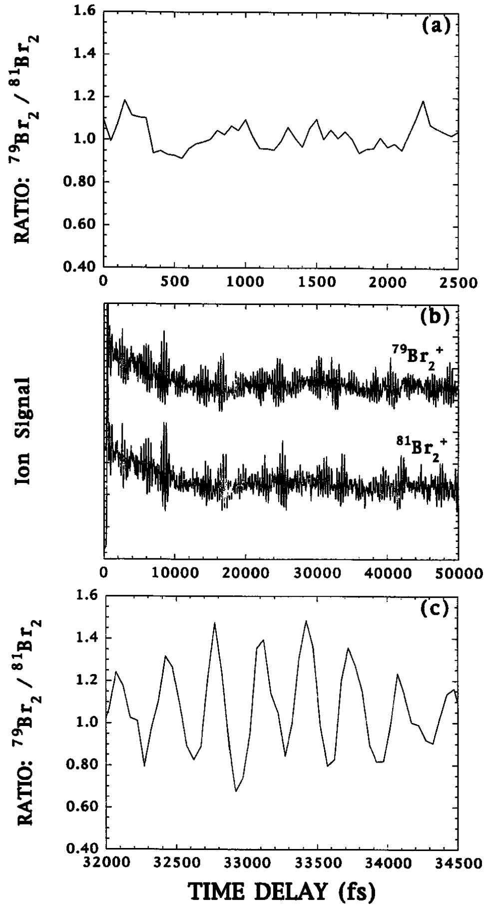

FIG. 3. Experimental demonstration of wave packet isotope separation showing the isotope ratio [$^{79}Br_2^+/^{81}Br_2^+$] as a function of the excitation-extraction pulse delay time. The natural abundance ratio is 1. (a) For times within the range 0–2.5 ps, the separation is poor as the wave-packets delocalize before they separate. (b) The $^{79}Br_2^+$ and $^{81}Br_2^+$ ion signals, collected simultaneously, are shown as a function of time over the range 0–50 ps, showing revival structure. The ion signal $^{79}Br_2^+$ is shifted for clarity. (c) The isotope ratio within the range 32–34.5 ps, corresponding to the point ($j = 4, k = 0$) of Fig. 2, is deeply modulated. The ratio varies by nearly 250% with a small change in extraction pulse delay, demonstrating the high single-step enrichment.

expect the current efforts of numerous groups on the controlled shaping of ultrashort laser pulses [24] to provide working tools for this new wavepacket technology which emerges at the classical-quantum border.

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*Present address: Department of Chemistry, Laser Centre Free University, Physical and Theoretical Chemistry, de Bolelaan 1083, 1081 HV Amsterdam, The Netherlands.

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