

Isotope separation using intense laser fields

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A laser-induced vibrational trapping mechanism is proposed for isotope separation in the $D_2^+ - H_2^+$ system interacting with an intense field. The theory is based on laser-induced quasibound states that can suppress the photodissociation of one of the isotopes, whereas the other still has a large dissociation rate. Such states, the existence of which has previously been evidenced, can be reached by appropriately adjusting laser parameters (wavelength and intensity). Great efficiency is expected for conveniently prepared initial vibrational states of a rotationless isotope and using a continuous-wave laser.

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Resonances play a major role in the dynamics of molecular processes induced by potential curve-crossing situations. Among typical examples, the analogy between *predissociation* and laser-induced *photodissociation* has repeatedly been emphasized [1,2]. It is basically the physical nature of interchannel couplings which differs from one case to the other: intramolecular for the former while radiative for the latter. Strong fluctuations in the widths (and lifetimes) of the resonances are commonly depicted, but much more surprising is the occurrence of vanishingly small widths (infinite lifetimes) for some special values of the couplings together with the energy positioning of the potentials. The existence of such bound states or resonances was first proved by Bandrauk and Child referring to semiclassical theory of electronic predissociation [3]. Their interpretation is based on a semiclassical evaluation of the poles of the scattering matrix. It originates from the quasicoincidence of a vibrational level supported by the closed diabatic potential, with a bound level supported by the attractive upper adiabatic potential which results from the diagonalization of the interchannel coupling. Such coincidences can clearly be considered as accidental in the sparse vibrational energy sequence of a given molecule. Their probability increases, however, with the density of states, when the rotation of the molecule is taken into account [4]. Predissociation in IBr offers an illustrative example with several coincidences occurring for different values of the rotational quantum number [5]. The situation is completely different for laser-induced resonances formed in photodissociation processes. More precisely, when the curve-crossing problem results from radiatively coupled field-dressed molecular states, coincidences may be obtained at will by properly adjusting the laser *wavelength* (i.e., the relative energy positioning of the potentials) and *intensity* (i.e., the strength of the coupling).

It has recently been shown that when studying molecu-

lar dissociation in intense short pulsed laser fields, although some low-lying vibrational levels dissociate 100%, for high-lying levels a significant stabilization is observed with non-negligible population remaining bound [6]. A possible explanation for this survival effect, which in some cases may lead even to the suppression of dissociation, is the trapping of portions of the initial vibrational wavepacket in the attractive well of the aforementioned upper adiabatic potential, which in turn return back to the uncoupled ground diabatic curve as the pulse settles down. It is tempting to bring together these two descriptions of stabilization by showing that trapping of the wavepacket can actually be associated with a coherent sum of laser-induced bound states [7,8]. An important and interesting feature concerning the coincidences which are responsible for the occurrence of these bound states is, for a given molecule, their great sensitivity with respect to laser characteristics (wavelength and intensity). It is precisely this sensitivity we are addressing in this work, as a very selective isotope separation technique. A coincidence obtained for a given system (molecule plus laser) does not hold when one proceeds to an isotopic substitution. The principal concern of this Rapid Communication is to bring evidence about the feasibility and the selectivity, as well as the efficiency of the D_2^+ versus H_2^+ isotope separation, using an intense laser field ($\approx 10^{13}$ W/cm²) to stabilize D_2^+ while dissociating H_2^+ .

In order to take full advantage of the stationary dressed-molecule picture that serves as an interpretative tool of the time-independent Floquet description of the electromagnetic field, we are hereafter referring to a continuous-wave (cw) laser. The molecular dissociation process is modeled by two electronic states (denoted g and u) in the Born-Oppenheimer approximation and the curve-crossing problem arises from the dressing of the corresponding potentials [9]. Two laser wavelengths are considered; namely, 120 and 95 nm, leading to a c^+ - or c^- -type of dissociation (i.e., crossing at the right or the left of the equilibrium position). In addition, both wavelengths are close to the maximum of the absorption line shape of H_2^+ ($\lambda \approx 115$ nm). Even for the relatively strong fields that will be used, this choice validates the rotating-

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wave approximation (RWA) in both its time-independent quantal and semiclassical versions [10]. We employ a J -conserving approximation, as has often been used in previous works [6].

The dressed-molecule potentials of D_2^+ , within these approximations and using a 120-nm wavelength laser of intensity $1.25 \times 10^{13} \text{ W/cm}^2$, are illustrated on Fig. 1 both in diabatic and adiabatic representations. As stated before, a resonance of zero width occurs when a diabatic level of turning points a_- and b_+ is close to an adiabatic level of turning points a_+ and b_+ (all turning points being associated with adiabatic potentials V_- and V_+). The destructive interference which results from this peculiarity can be interpreted [11] through Child's diagrammatic method [12] depicted as an inset of Fig. 1, where the lines carrying the arrows indicate the adiabatic channel JWKB wave functions. The boxes designate the splitting and mixing operations undergone by the wavelets reaching the avoided crossing R_c . The Gamow-Siegert criterion for a resonance consists in imposing a zero incoming amplitude to the open channel V_- , i.e., $V''_- = 0$. The corresponding outgoing amplitude V'_- that we are interested in results from reflections of the wavelets at the left (a_+ and a_-) and right (b_+) turning points and from their mixing around R_c . For an elementary step, where an amplitude \tilde{V}'_+ is deposited in channel V_+ at R_c and undergoes a unique reflection at b_+ , followed by reflections at a_+ after a channel mixing at R_c , one gets an amplitude \tilde{V}'_- [13,14]:

$$\tilde{V}'_- = -e^{-\pi\nu}(1 - e^{-2\pi\nu})^{1/2} e^{-i\chi} [e^{2i(\alpha_+ + \beta_+ + \chi)} - e^{2i(\alpha_- + \beta_+)}] \tilde{V}'_+ . \quad (1)$$

The phase factor χ varies from $-\pi/4$ (weak-field limit) to 0 (strong-field limit) [11], and is given in terms of ν [13,14], which, for weak-field situations or constant (i.e., R -independent) radiative couplings, is merely the

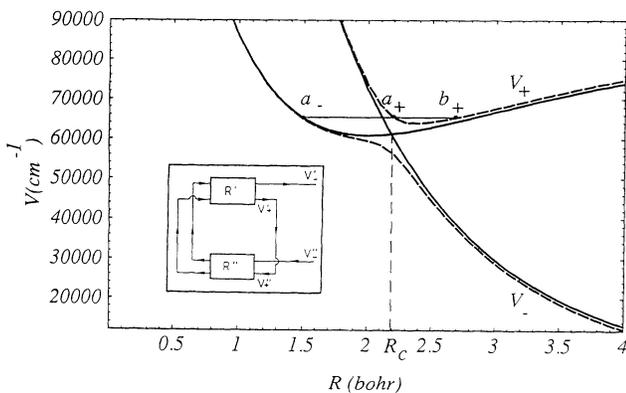


FIG. 1. Diabatic (solid lines) and adiabatic (dotted lines) potential curves of the reference block of D_2^+ , for a laser wavelength 120 nm and intensity $1.25 \times 10^{13} \text{ W/cm}^2$. The ground electronic state is dressed by the photon energy. The resonance position corresponding to the coincidence $\nu_2=2$, $\nu_+=0$ is marked by a thin line. a_- , a_+ , and b_+ denote the classical turning points. The corresponding Child semiclassical diagram (see Ref. [14]) is shown as an inset.

Landau-Zener parameter [1]. Other energy-dependent phase factors of Eq. (1) are

$$\alpha_{\pm} = \int_{a_{\pm}}^{R_c} k_{\pm}(R) dR, \quad \beta_+ = \int_{R_c}^{b_+} k_+(R) dR, \quad (2)$$

$k_{\pm}(R)$ being the wave numbers associated with $V_{\pm}(R)$.

A vanishing outgoing amplitude in the open channel means that the resonance has an infinite lifetime, its width being precisely given by [11,15]

$$\Gamma = \frac{\hbar^2}{2m} k_- |V'_-|^2, \quad (3)$$

where V'_- results from the summation of all the elementary steps described by Eq. (1) and m is the reduced mass. The two exponentials of Eq. (1) compensate each other, leading to $V'_- = 0$, if the following conditions are fulfilled:

$$\alpha_+ + \beta_+ + \chi = (v_+ + \frac{1}{2})\pi, \quad \alpha_- + \beta_+ = (v_2 + \frac{1}{2})\pi, \quad (4)$$

with integer values for ν_+ and ν_2 . These conditions are close to stating that the energy is that of a vibrational bound state of the adiabatic $V_+(R)$ or the ground diabatic potential. A complete semiclassical analysis provides the approximate expression for the resonance width [13,14]:

$$\Gamma = \frac{\pi}{\hbar} (e^{2\pi\nu} - 1) \frac{[\omega_+^2 + \omega_2^2 (e^{2\pi\nu} - 1)]}{[\omega_+ + \omega_2 (e^{2\pi\nu} - 1)]^3} (E_{\nu_2} - E_{\nu_+})^2, \quad (5)$$

ω_2 and ω_+ being the local energy spacings. This equation gives the lowest-order formula in terms of the energy differences involved, indicating that a coincidence between the ν_+ adiabatic level (of energy E_{ν_+}) and the ν_2 diabatic level (of energy E_{ν_2}) leads to a laser-induced quasibound state and, therefore, to suppression of dissociation. Such states of zero width may serve as an interpretative tool when describing trapping mechanisms in the $V_+(R)$ closed adiabatic channel. Apart from this interpretative approach, which labels the quasibound level, the semiclassical theory can also be invoked to adjust, at least approximatively, laser parameters (wavelength and intensity) so as to guide exact quantum calculations. These are done by solving the close-coupled equations of the time-independent Floquet Hamiltonian and by imposing the Gamow-Siegert end-point conditions within the framework of the complex rotation of the coordinate [16,17]. Converged results within eight digits of accuracy are obtained by taking into account three Floquet blocks in addition to the reference one, giving rise to five open and three closed channels.

As stated before, the two laser wavelengths under consideration illustrate two distinct curve-crossing situations, i.e., c^+ -type for $\lambda=120 \text{ nm}$ (as in Fig. 1) and c^- -type for $\lambda=95 \text{ nm}$. Using a semiclassical approach the first occurrence, for D_2^+ , of a diabatic versus adiabatic level coincidence is $\nu_2=2$, $\nu_+=0$ for $\lambda=120 \text{ nm}$, whereas for $\lambda=95 \text{ nm}$, the possibility still exists to fulfill the same condition for a lower diabatic level $\nu_2=1$, $\nu_+=0$, but by increasing the intensity. The semiclassically estimated critical field strengths leading to coin-

TABLE I. Critical intensities I (in W/cm^2) leading to laser-induced quasibound levels for H_2^+ and D_2^+ for two wavelengths λ . Semiclassical estimates are given for both $\chi=0$ (strong-field limit) and for $\chi=\chi_{\text{LZ}}$ corresponding to the Landau-Zener value. Quantum results are presented within both a single Floquet block RWA approximation and resulting from converged multiblock calculations. Numerical difficulties render inaccurate the determination of the critical intensity for H_2^+ at $\lambda=120$ nm.

| λ (nm) | Isotope | Critical intensities I (10^{13} W/cm^2) | | | |
|----------------|----------------|---|-------------------------|---------|-------|
| | | Semiclassical | | Quantal | |
| | | $\chi=0$ | $\chi=\chi_{\text{LZ}}$ | RWA | Exact |
| 120 | D_2^+ | 1.50 | 1.25 ^a | 1.11 | 1.11 |
| | H_2^+ | 3.40 | 3.10 | 2.79 | |
| 95 | D_2^+ | 3.00 | 2.81 ^b | 2.14 | 2.14 |
| | H_2^+ | 5.20 | 4.60 | 3.57 | 3.59 |

$${}^a\chi_{\text{LZ}} = -0.2422.$$

$${}^b\chi_{\text{LZ}} = -0.1568.$$

cidences are indicated on Table I for two values of the phase correction factor; namely, $\chi=0$ and χ_{LZ} given by the familiar Landau-Zener approximation. The intensities are of the order of magnitude of 10^{13} W/cm^2 typically pertaining to a strong-field regime. The Landau-Zener absolute values of χ_{LZ} , for D_2^+ , are decreasing when going from $\lambda=120$ nm ($\chi_{\text{LZ}}=-0.242$) to $\lambda=95$ nm ($\chi_{\text{LZ}}=-0.157$), as the critical intensity has to increase by a factor of 2 (from 1.25×10^{13} W/cm^2 for $\lambda=120$ nm to 2.81×10^{13} W/cm^2 for $\lambda=95$ nm). Although systematically larger for $\chi=0$, the two estimates of the critical intensities do not differ by more than 15%. The insets of Figs. 2(a) (for $\lambda=120$ nm) and 2(b) (for $\lambda=95$ nm) display, on an enlarged intensity scale, the variation of the resonance width in the vicinity of the critical intensities for D_2^+ . The results of three types of calculations are plotted: semiclassical [i.e., Eq. (5) with Landau-Zener approximation], quantal within the RWA by referring to but one Floquet block, and multi-Floquet block converged quantal. They can be summarized as follows.

(i) The semiclassical approach systematically leads to vanishingly small widths for larger intensities as compared to the quantal approaches. However, as can be seen from Table I, the differences remain reasonably small.

(ii) RWA (single-Floquet block close-coupled calculation) turns out to be valid when compared with the exact converged quantal calculation for both wavelengths. This is basically due to the fact that both wavelengths are close to the top of the one-photon absorption line shape. In particular, the critical intensities reached by the RWA or exact calculations are nearly identical (see Table I), clearly supporting the fact that for these wavelengths, the reference Floquet block is the one responsible for the suppression of the dissociation.

(iii) The curvature for the width considered as a function of the intensity near the zero minimum for $\lambda=95$ nm

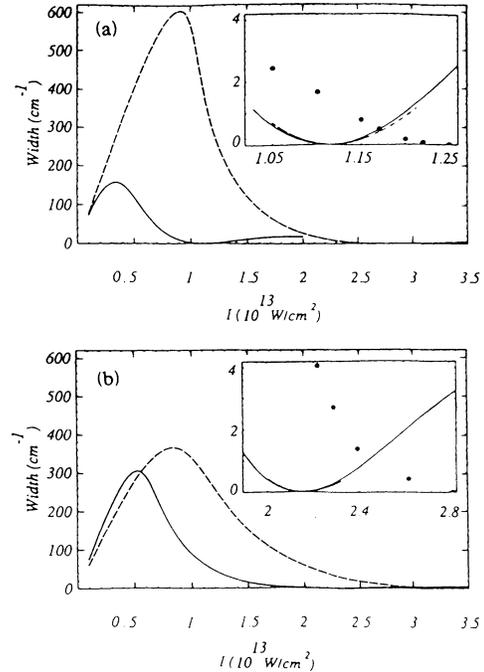


FIG. 2. (a) The $v_2=2$ resonance width (in cm^{-1}) as a function of the laser intensity (in W/cm^2), for a 120-nm wavelength. Solid line, D_2^+ dissociation rate; dashed line, H_2^+ dissociation rate. The inset corresponds to D_2^+ dissociation in the vicinity of the critical intensity. Dots, semiclassical approximation; solid line, single Floquet block approximation; dashed line, converged quantal calculation. (b) Same as for (a) but referred to the $v_2=1$ resonance for a 95-nm wavelength.

is 3×10^{-25} cm^3/W^2 , which can be related to the robustness of the phenomena. A variation of 10% of the intensity induces a variation of less than 1 cm^{-1} for the width.

Figures 2(a) and 2(b) offer a comparative overview, on a wider scale, of the intensity dependence of widths of D_2^+ and H_2^+ . Such different behaviors of isotopes with respect to the field strength, putting particular emphasis on stabilization and rotational effects, have already been discussed by McCann and Bandrauk [18,19] in the case of Li_2 multiphoton dissociation, with laser intensities ranging around 10^{11} W/cm^2 . The following comments are in order.

(i) In the weak-field regime ($I < 10^{12}$ W/cm^2) the widths behave linearly with respect to the intensity. For $\lambda=120$ nm the dissociation rate of H_2^+ dominates over that of D_2^+ , while a reverse situation is depicted for $\lambda=95$ nm.

(ii) Optical nonlinearities appear for stronger field strengths [2]. A maximum for the dissociation rate is reached at $I \approx 4 \times 10^{12}$ W/cm^2 and $I \approx 10^{13}$ W/cm^2 for D_2^+ and H_2^+ , respectively, at $\lambda=120$ nm. The corresponding values at $\lambda=95$ nm are $I \approx 6 \times 10^{12}$ W/cm^2 and $I \approx 1.1 \times 10^{13}$ W/cm^2 .

(iii) The strong-field behavior is dominated by an overall decrease toward zero for both D_2^+ and H_2^+ and for both wavelengths. The near-zero behavior for D_2^+ has already been examined in detail [insets of Figs. 2(a)

and 2(b)]. A similar situation holds for H_2^+ , the minima occurring now at $I \approx 2.8 \times 10^{13} \text{ W/cm}^2$ ($\lambda = 120 \text{ nm}$) and $I \approx 3.6 \times 10^{13} \text{ W/cm}^2$ ($\lambda = 95 \text{ nm}$). These values, together with their semiclassical estimates, are gathered in Table I. An increasing behavior, for both D_2^+ and H_2^+ , is again observed for intensities exceeding $3.6 \times 10^{13} \text{ W/cm}^2$.

But obviously the most important information is that the zero minima of D_2^+ correspond, for both wavelengths, to a rather large width of H_2^+ , namely $\Gamma \approx 600 \text{ cm}^{-1}$ (for $\lambda = 120 \text{ nm}$) and $\Gamma \approx 100 \text{ cm}^{-1}$ (for $\lambda = 95 \text{ nm}$). In other words, we are showing that one can proceed to a specific choice for a laser wavelength and intensity such that D_2^+ dissociation may completely be suppressed, whereas for the same field H_2^+ is still dissociating fast.

We would finally like to comment about the rotational effects that are thoroughly discussed in Refs. [18,19] as applied to our particular isotope separation model. Starting from molecules in their ground electronic rotationless state $|g, J=0\rangle$ (some of them, taken from an initial distribution, will bear these characteristics), the field-induced rotational coupling involves a sequential decay process, i.e.,

$$|g, J=0\rangle \rightarrow |u, J=1\rangle \rightarrow |g, J=2\rangle \\ \rightarrow |u, J=3\rangle \rightarrow \dots$$

Clearly, if for some specific laser parameters, the first step

of this mechanism is inhibited, $|g, J=0\rangle$ is a quasibound state leading to a vanishing total width. Schematically this situation is identical to that illustrated in insets of Figs. 2(a) and 2(b), where the trapping mechanism for a given intensity within a unique Floquet block induces a zero total decay rate for the more general multiblock model, although slight differences occur for other values of the intensity. Since not all molecules are necessarily in their $J=0$ state, the relative importance of rotational excitations will contribute to the *yield* but not to the *efficiency* of the isotope separation scheme.

As a word of conclusion, we have evidenced the possibility of an isotope separation (D_2^+ - H_2^+) based on a vibrational trapping mechanism. Great efficiency is expected for properly prepared initial vibrational states of a rotation free isotope interacting with a cw laser. Work is under progress in our group to relax some of these constraints.

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