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Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/1.472745

Publication date:
1996

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):

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Two-pulse laser control of bond-selective fragmentation

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(Received 11 June 1996; accepted 22 August 1996)

We elaborate on a two-pulse (pump-pump) laser control scheme for selective bond-breaking in molecules [Amstrup and Henriksen, J. Chem. Phys. 97, 8285 (1992)]. We show, in particular, that with this scheme one can overcome the obstacle of intramolecular vibrational relaxation. As an example, we consider an ozone molecule with isotopic substitution, that is, $^{16}$O$^{16}$O$^{18}$O. It is shown that asymmetric bond stretching can be created in simple (intense) laser fields. We predict that an alternating high selectivity between the channels $^{16}$O$+^{16}$O$^{18}$O and $^{16}$O$^{18}$O$+^{18}$O can be obtained when such a non-stationary vibrating ozone molecule is photodissociated with short laser pulses ($\sim$10–15 fs) with a time delay corresponding to half a vibrational period ($\sim$17 fs).

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I. INTRODUCTION

Control of molecular dynamics at the microscopic level is a subject of much current interest. Control of bond-breaking and bond-formation are the objectives most pertinent to chemistry. The first of these objectives—the control of bond-breaking—is most easy to envision. To that end one can consider a unimolecular process where the initial nuclear geometry is well-defined, that is, it is only limited by the quantum mechanical uncertainty. The question we are considering is how to change the branching ratio between chemically distinct channels, say for a triatomic ABC molecule, between $A + BC$ and $AB + C$.

One approach is to try to induce selective bond-breaking via infrared multiphoton excitation (see Refs. 1–4 and references therein). It has been demonstrated that with a properly designed laser pulse one can overcome the obstacle of intramolecular vibrational relaxation (IVR) between bonds in a molecule.4 A general obstacle with infrared multiphoton excitation is, however, that laser pulses with very high intensity can be required in order to obtain a detectable dissociation probability. Thus competition with molecular ionization may be a problem.

Alternatively, we can consider photofragmentation in the ultraviolet part of the spectrum, that is, fragmentation is induced via an electronic transition. We will, in the following, limit the discussion to such processes and to molecules where one of the electronically excited states is purely repulsive, such that direct fragmentation can take place in that state.

One way to accomplish control is to explore the full dynamics embodied in the Franck–Condon principle (although originally formulated in a semiclassical framework, the principle is, when interpreted properly, fully quantum mechanical1). This approach is termed passive control.5,6 The branching ratio varies as a function of the photon energy and the initial (vibrational) excitation in accordance with the Franck–Condon factors. In practice, it can be explored via a set-up with two lasers in the cw regime. The first laser prepares an excited vibrational eigenstate and the molecule is dissociated with a second laser via an excitation to the repulsive electronic state. A nice example is provided by the photodissociation of HOD in the first electronically excited state. The vibrational eigenstates of the electronic ground state are, essentially, local modes in the OH or OD stretch. If, e.g., an excited OH eigenstate is populated in HOD, an enhanced branching into the channel $H + OD$ is observed in a subsequent photodissociation process.7–11 However, the branching ratio between $H + OD$ and $D + OH$ depends on the frequency of the second laser and high selectivity can be obtained only in a narrow frequency region. This frequency region is broadened when the initial vibrational excitation is increased but is still relatively narrow even at high vibrational excitation. Furthermore, it is clear that in this scheme one takes advantage of the fact that in some molecules, the vibrational eigenstates are of the local mode type and pre-excitation into these states directs the fragmentation into the desired channel. Thus the scheme is not expected to work for molecules where the vibrational eigenstates are normal mode-like.

There are ways to circumvent these obstacles, that is, the limitations of passive control—the schemes are termed active control schemes.5,6 One approach is to use a control scheme for unimolecular reactions which has been introduced by Brumer and Shapiro.12,13 In the simplest form it is also based on two lasers in the cw regime where the lasers, via two different routes, can take the molecule into the electronically excited state. It is, in addition, assumed that the phase difference between these laser fields is controllable. This translates into a phase dependent interference term in the dissociation probability which can be controlled by virtue of the experimental control over the phase difference. For fragmentation of HOD via the first electronically excited state it was shown that the branching ratio between the two chemical channels could be affected and improved in this way.14

Another approach, and the scheme we will consider in this paper was introduced a couple of years ago.5,15 It is in the spirit of the “pump-dump” scheme of Tannor and Rice16,17 (see also Ref. 6 and references therein). Two lasers are required—an intense laser in the infrared region which creates a superposition of vibrational eigenstates—and a
second short laser pulse in the ultraviolet region which takes the molecule into the dissociative state, at an appropriate time delay between the pulses, e.g., when the wave packet created with the first pulse is positioned exclusively in the exit channel of the dissociative state. This scheme has also been applied to HOD\(^{15}\) and complete selectivity between the exit channel of the dissociative state. This scheme has also created with the first pulse is positioned exclusively in the molecule into the dissociative state, at an appropriate number of symmetric or asymmetric stretch eigenstates in this molecule, the dissociative dipoles, etc., is available.

The question we are considering in this paper is: Can we control bond-breaking for a, basically, symmetric molecule where the vibrational eigenstates are normal mode-like? — or in an alternative formulation — in HOD the IVR is negligible (even at very high excitation) what if we consider a molecule where IVR is important? (note that, in principle, one can design laser fields such that energy stays localized in a given bond, however, what is required is a field which gradually takes the form of a constant field\(^{19}\) with such a high field strength, that it might be unrealistic in practice). We will in this paper show that the control of bond-breaking within the framework of the two-pulse (pump-pump) scheme, in principle, is equally straightforward whether IVR is important or not.

We illustrate this proposition with an example, an ozone molecule with isotopic substitution, that is, \(^{16}\text{O}^{16}\text{O}^{18}\text{O}\) (where information about potential energy surfaces as well as dipole surfaces, etc., is available). Due to the near symmetry of the vibrational eigenstates in this molecule, the dissociation out of any of the symmetric or asymmetric stretch eigenstates will give about the same probability for the two channels, that is, \(^{16}\text{O}^{16}\text{O}^{18}\text{O}\) or \(^{16}\text{O}^{16}\text{O}^{16}\text{O}\). This paper is organized in the following way: In section II the Hamiltonian of ozone in a laser field is defined and the numerical technique used in order to solve the time-dependent Schrödinger equation is briefly described. The vibrational dynamics of the electronic ground state induced by infrared multiphoton excitation as well as the subsequent nuclear dynamics in the second (dissociative) electronically excited state induced by a short ultraviolet pulse is presented and discussed in section III.

II. COMPUTATIONAL APPROACH

We use here, basically, the same approach as for the water molecule.\(^{15}\) The basic approximation (in order to make the quantum calculation tractable) is that bending as well as the rotational degrees of freedom are neglected. This approximation can be justified. Thus for HOD in the electronic ground state, the vibrational energy levels with zero quanta of excitation in the bending degree are well described by model potentials where the bending angle is fixed (see Ref. 15 and references therein). This suggests that coupling between the stretching and the bending degrees of freedom is weak and that the bending motion can be left out when one considers the vibrational dynamics induced by a laser with a frequency which is well above the (low) bending frequency.

That this proposition is appropriate has been confirmed directly in calculations where the bending degree of freedom was included.\(^ {20}\) The bending degree of freedom of the first excited electronic state can be neglected due to the weak anisotropy of the water potential.

For \(\text{O}_3\) in the electronic ground state, at least, the lowest vibrational energy levels with zero quanta of excitation in the bending degree are again well described by model potentials where the bending angle is fixed (see Ref. 21 and references therein). The bending degree of freedom of the second excited electronic state of ozone is, however, not inactive during the dissociation.\(^ {22}\) Thus the bending angle has decreased about 10 degrees after the first 10 fs and decreases further as the dissociation process proceeds. The branching ratio is, however, essentially controlled by short time dynamics. That is, it is established in less than 10 fs when dissociation is initiated with a \(\delta\)-pulse — the extremely small recurrence in the wave packet motion when the bending is included\(^ {22,23}\) will not influence the branching ratio in a noticeable way. Thus when only short pulse excitation is considered, we believe that qualitatively correct (if not almost quantitatively correct) results for the branching can be obtained also when the bending degree of freedom is fixed at the equilibrium value of the ground state.

We consider, as explained above, a two degree of freedom model of \(^{16}\text{O}^{16}\text{O}^{18}\text{O}\) where bending and rotation are neglected. The coordinates describing the \(^{16}\text{O}^{18}\text{O}\) and \(^{16}\text{O}^{16}\text{O}^{16}\text{O}\) bonds are denoted by \(r_1\) and \(r_2\), respectively. The associated conjugate momenta are \(p_1\) and \(p_2\). The internal kinetic energy operator is given by (see, e.g., Ref. 24)

\[
\hat{T} = \frac{\hat{p}_1^2}{2\mu_1} + \frac{\hat{p}_2^2}{2\mu_2} + \frac{\hat{p}_1\hat{p}_2}{2m(16\text{O})}\cos\theta, 
\]

where

\[
\hat{\rho}_j = \frac{\hbar}{i} \frac{\partial}{\partial r_j}, \quad j = 1, 2,
\]

\[
\mu_1 = m(18\text{O})m(16\text{O})/(m(18\text{O}) + m(16\text{O})),
\]

\[
\mu_2 = m(16\text{O})m(16\text{O})/(m(18\text{O}) + m(16\text{O})),
\]

and \(\theta\) is the fixed bending angle of 116.8 degrees.

Two electronic states are considered: the electronic ground (\(X\)) state and the second excited (\(B\)) state. An intense laser in the infrared (ir) region and a laser in the ultraviolet (uv) region of the spectrum are interacting with the molecule. The time evolution associated with the nuclear motion can then be calculated from the time-dependent Schrödinger equation,

\[
i\hbar \frac{\partial}{\partial t} \left( \begin{array}{c} \psi_g \\ \psi_e \end{array} \right) = \left( \begin{array}{cc} \hat{H}_g + \hat{H}_{ir} & \hat{H}_{av} \\ \hat{H}_{av} & \hat{H}_e \end{array} \right) \left( \begin{array}{c} \psi_g \\ \psi_e \end{array} \right),
\]

where \(\psi_g = \psi_g(r_1, r_2, t)\) and \(\psi_e = \psi_e(r_1, r_2, t)\) are the wave functions associated with nuclear motion in the ground and second excited state, respectively. \(\hat{H}_g = \hat{T} + V_g\) and \(\hat{H}_e = \hat{T} + V_e\) are the nuclear Hamiltonians in the two states. \(\hat{H}_{ir}\) and \(\hat{H}_{av}\) to be specified below, describe the interaction between the molecule and the two lasers.
Equation (3) was solved numerically on a two-dimensional grid by a split operator (SPO) method\textsuperscript{25,26} that uses the grid method and the fast Fourier transform algorithm for the evaluation of the effect of the kinetic operator. The vibrational eigenstates of the electronic ground state were calculated by the method of Kosloff and Tal-Ezer\textsuperscript{27} through integration of the time-dependent Schrödinger equation in imaginary time.

The potential energy surfaces used here are the \textit{ab initio} potentials from Ref. 22 fitted to the Murrell–Sorbie (see also Refs. 28 and 29) analytical function. Note that there is a few errors ($C_{002} \rightarrow C_{020}$, $C_{102} \rightarrow C_{120}$, $C_{301} \rightarrow C_{310}$) in Table II of Ref. 22. For the equilibrium structure of the $X$ state, the experimental geometry was used,\textsuperscript{22} i.e., the equilibrium bond distance is 2.4018 $a_0$.

The dipole moment surface of the electronic ground state is taken from Ref. 30. The ir-Hamiltonian, $\hat{H}_{\text{ir}}$, is given by

$$\hat{H}_{\text{ir}} = \mu_{\text{ir}} \cdot \mathcal{E}_{\text{ir}}.$$  

Here, $\mu_{\text{ir}}$ is the ir-dipole moment vector with the two components, $\mu_x$ and $\mu_y$, along the bisector of the two bonds and perpendicular on that direction, respectively, and $\mathcal{E}_{\text{ir}}$ is the ir electric field vector.

As in Ref. 22 we consider only the symmetric component of the $X \rightarrow B$ transition dipole moment. The uv-Hamiltonian, $\hat{H}_{\text{uv}}$, is given by

$$\hat{H}_{\text{uv}} = \mu_{\text{uv}} \cdot \mathcal{E}_{\text{uv}}.$$  

Here, $\mu_{\text{uv}}$ is the symmetric component of uv-dipole moment.

FIG. 1. Calculated vibrational eigenstates on the ground electronic surface using the Sheppard–Walker potential (Ref. 32). Contours are "from 0.4 and up" (solid) and "from –0.4 and down" (dashed). The numbers in the upper left corner are the associated energies (in cm$^{-1}$).
vector which is in the molecular plane and perpendicular to the bisector of the two bonds and $E_{uv}$ is the uv electric field vector.

For the laser pulses we consider the chirp expression of an electric field with an initially Gaussian pulse shape. Here we shall only consider second order chirp since the zeroth and first order chirp could be included in a phase factor and a time delay, respectively. For zero higher than second order chirp, we have the following result:

$$\mathcal{E}(t) = \text{Re} \left( \mathcal{E}_{\text{max}} \sqrt{\frac{2 \pi \tau}{\tau + 2iz\beta^2}} e^{-i(\tau + 2iz\beta^2)} \right).$$  \hspace{1cm} (6)

The above expression reflects a possible experimental realization of the pulse: It can be achieved by propagating a Gaussian pulse through a medium of length $z$ with a frequency dependent propagation factor $\beta$ (e.g., an optical fiber, see Ref. 31).

The instantaneous frequency of the field (which is the time derivative of the phase) is

$$\omega_c(t) = \frac{d \arg(\mathcal{E}(t))}{dt} = \omega_0 + \alpha t,$$  \hspace{1cm} (7)

where $\alpha = 4z\beta^2/(\tau^2 + 4(z\beta^2)^2)$. Note that $t$ should be replaced by $t - t_c$ in the equations when we consider a pulse centered at $t = t_c$.

The length of the pulse depends on the chirp, and the FWHM (full width at half maximum) of the electric field and the intensity are

$$\text{FWHM}_{\text{el,fi.}}^{(2)} = 4 \ln 2 \left( \tau + 4(z\beta^2)^2 \right)/\tau,$$  \hspace{1cm} (8)

and $\text{FWHM}_{\text{int.}}^{(2)} = \text{FWHM}_{\text{el,fi.}}^{(2)}/2$, respectively. The FWHM of the squared frequency spectrum is independent of the chirp and is given by

$$\text{FWHM}_{\text{int.}}^{(2)} = \frac{8 \ln 2}{\tau} = \frac{4 \ln 2}{\text{FWHM}_{\text{int.}}^{(2)=0}}.$$  \hspace{1cm} (9)

III. RESULTS AND DISCUSSION

Figure 1 shows the first six vibrational eigenstates of the electronic ground state. They can, essentially, be classified as pure symmetric stretch or pure asymmetric stretch modes (state number five is a combination). Thus the wave functions and, especially, the energies differ only slightly from the results obtained for normal ozone where we obtain energies which are in good agreement with experimental values$^{21}$ (the deviation is less than 3% for the states considered here). Note that the two modes come in pairs which are closely spaced in energy. This implies that selective excitation of these states with an intense laser pulse is difficult.

In order to evaluate the coupling between an ir-laser and the molecule, we need the dipole moment of the ground state as shown in Fig. 2. Note that the derivative in the Franck–Condon region is larger for $\mu_x$ than for $\mu_y$. This implies that with a given electric field the asymmetric stretch mode is more readily excited than the symmetric stretch mode.

The idea is now to apply an intense laser in the infrared region in order to create a superposition of the vibrational eigenstates. That is, to create forced vibrations in the molecule with the laser. In Fig. 3, we show the expectation values of the bond lengths for a vibrational state created with an intense ir-pulse with the parameters specified in the figure text. Note that the electric field amplitude corresponds to an intensity of about 10 TW/cm$^2$ and that a field with a small negative chirp is employed (this is, however, not essential in the present situation). The angle between the electric field vector and the $\mu_x$ component of the dipole moment is fixed at 45 degrees in order to mimic a coupling which is relevant for a molecule with a random orientation. The excitation corresponds, essentially, to a pure asymmetric stretch, however, with a small contribution from the symmetric stretch motion. The smallness of this contribution is due to the small derivative of $\mu_x$. The absence of symmetric stretch motion (according to Fig. 3) over the first 200 fs implies, furthermore, that energy transfer into the symmetric stretch mode is negligible.

The associated vibrational wave packet is shown for $t = 130$ fs and $t = 147$ fs in Fig. 4. These two configurations correspond to turning points of the asymmetric stretch vibration. The time difference (17 fs) is, approximately, one half.
of a vibrational period for the asymmetric stretch vibration. It should be noted that as a general trend the wave packet is spreading but, at the turning points, the wave packet is still well localized on a time scale of several vibrational periods. In HOD with the very light masses, wave packet spreading was much faster.

We now turn on the second (uv) laser and considered the branching ratio between the two chemical channels. Figure 5 shows the branching ratio, \( P_{12} = P_1 / P_2 \), between channel (1): \( ^{16}\text{O}^{16}\text{O} + ^{18}\text{O} \) and (2): \( ^{16}\text{O} + ^{16}\text{O}^{18}\text{O} \) for uv-pulses centered at various times and as a function of the pulse length (with a fixed ir-pulse centered at \( t_c = 90 \) fs, as specified above). The parameters specifying the uv-pulses are given in the figure text. The figure shows the logarithm of \( P_{12} / 0.87 \), where the number 0.87 is the branching ratio obtained for dissociation out of the vibrational ground state with a \( \delta \)-pulse, that is, the bonds are broken with about equal probability in this case. Bond-breaking corresponding to channel (2) is slightly favoured due to the smaller reduced mass which initially gives a wave function which is more delocalized along this channel.

Thus branching ratios which are substantially larger or smaller than 0.87 is obtained with the two-pulse scheme. The highest branching ratios obtained with pulses with a width of 2, 5, 10, and 15 fs are 4.3, 4.2, 3.3, and 2.6, respectively. The smallest branching ratios obtained with the same pulses are 0.12, 0.16, 0.22, and 0.32, respectively. We observe that the highest selectivity is obtained when the uv-pulse is centered at times such that the pulse transfers the wave packet to the dissociative state prior to the time where the asymmetric vibration reach the turning points. Thus the optimal timing of the second pulse depends on the position as well as the momentum of the ground state wave packet. It is, accordingly, important to stress that the selectivity in the pump-pump scheme is a function of the ground state wave packets position in configuration space but its position in momentum space may be equally important.

FIG. 3. Expectation values and associated uncertainties (in atomic units) of the two bond lengths under the influence of a slightly chirped ir-laser. The electric field has the following characteristics: maximum amplitude \( E_{\text{max}} = 0.02 \) a.u., center of pulse \( t_c = 90 \) fs, center frequency \( \omega_0 = 0.00468 \) a.u., width \( \text{FWHM}_{t_c} = 50 \) fs, and linear chirp \( \alpha = -25000 \) a.u. \( \omega = -13.7 \) ps \(^{-2} \) [see Eq. (7)]. The angle of the electric field with respect to the x-axis is 45 degrees. Note that the expectation value of the equilibrium bond length \( (r=0) \) is larger than 2.40 \( a_0 \) and that this is a signature of the anharmonicity of the potential.

FIG. 4. Contour plot of the wave function numerically squared after 130 fs (A) and 147 fs (B) under the influence of the same ir-laser as in Fig. 3. Contour values are 2, 4, 6, \ldots
Control within the framework presented in this paper appears to be possible for a fairly large class of molecules. It should, however, be noted that, so far, we have only considered control for direct fragmentation processes. Furthermore, that the experimental implementation obviously, at present, is limited by the availability of laser pulses with pulse lengths of the order of a vibrational period.

ACKNOWLEDGMENT

This work was supported by the Danish Natural Science Research Council.


FIG. 5. The branching ratio between the two chemical channels for u pulses centered at various times in the interval from 120 to 150 fs and for pulse lengths (FWHM el. fi.) of 2.5, 10, and 15 fs, respectively. $P_{2s}$ is the branching ratio between the two channels (defined in the text) and the number 0.87 is the branching ratio obtained for dissociation out of the vibrational ground state with a $d$ pulse. The maximum amplitude of the electric field is $E_{\text{max}} = 0.0005$ a.u. and the center frequency $\omega_0 = 40,000$ cm$^{-1}$.