Controlling vibrational wave packet motion with intense modulated Laser Fields

Niikura, Hiromichi; Corkum, Paul; Villeneuve, D.

National Research Council Canada   Conseil national de recherches Canada

Canada

Controlling Vibrational Wave Packet Motion with Intense Modulated Laser Fields

Hiromichi Niikura, P. B. Corkum, and D. M. Villeneuve

National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

Intense, nonresonant laser fields produce Stark shifts that strongly modify the potential energy surfaces of a molecule. A vibrational wave packet can be guided by this Stark shift if the laser field is appropriately modulated during the wave packet motion. We modulated a 70 fs laser pulse with a period on the time scale of the vibrational motion (~ 10 fs) by mixing the signal and idler of an optical parametric amplifier. We used ionization of H_2 or D_2 to launch a vibrational wave packet on the ground state of $H_2{}^+$ or $D_2{}^+$. If the laser intensity was high as the wave packet reached its outer turning point, the Stark shift allowed the molecule to dissociate through bond softening. On the other hand, if the field was small at this critical time, little dissociation was measured. By changing the modulation period, we achieved control of the dissociation yield with a contrast of 90%.

Strong nonresonant laser fields can apply forces to molecules that are comparable to the valence electron's binding energy. This leads to very large Stark shifts [1,2] that depend on the field, the internuclear separation [3], and on the alignment with respect to the laser polarization. By controlling the laser intensity, we control the Stark shifts, allowing us to guide the nuclear motion of the molecule. This kind of control has already been exercised over the rotational motion of molecules [4,5], where it was shown that a molecule could be spun so fast that it dissociates by the centrifugal force.

We demonstrate that *vibrational* wave packets can be controlled, leading to selective molecular dissociation, if the laser field is modulated on the same time scale as molecular motion. We modulate a 1.6 μm, 70 fs laser pulse with that time scale, which in turn modifies the potential energy surfaces during molecular motion. The electronic energy levels of the molecules respond rapidly to the laser field oscillations, but the nuclei respond only to the cycle-averaged Stark shift. The vibrational wave packet moves on these field-modified potential energy surfaces [1] [Fig. 1(a)]. Controlling the temporal structure of the laser pulse envelope allows us to shift the potential energy at just the right time and by just the right amount to guide a vibrational wave packet to dissociation.

We use H_2 and its isotope D_2 as precursor molecules, demonstrating control over the vibrational wave packet motion of their ions. The vibrational period of $H_2{}^+$ ($X\,{}^2\Sigma_g$) and $D_2{}^+$ ($X\,{}^2\Sigma_g$) is ~ 16 and ~ 22 fs, respectively, in field-free conditions [6] at the most probable vibrational eigenstate of $\nu = 2$. To change the intensity of the laser field on that time scale, we combine pulses with differing frequencies that are well below any electronic transition energies in the molecule. The two frequencies are generated by an optical parametric amplifier (OPA) pumped by a femtosecond Ti:sapphire laser. The two frequencies sum to the Ti:sapphire frequency. The beat frequency, given by half the difference of the two fre-

quencies, can be adjusted by controlling the OPA's wavelength tuning [see Fig. 1(b)].

The modulated infrared laser pulse plays two roles in our experiment. First, it launches the vibrational wave packet by ionization of the neutral molecule [7]. Since the probability of tunnel ionization is highly nonlinear as a function of laser intensity, ionization will occur near the peak of the envelope. Thus, we launch the wave packet at a well-defined time during the beat. Second, it guides the vibrational wave packet and gates photodissociation. This happens because the wave packet moves on the field-modified surfaces [Fig. 1(a), dashed curve], which we control. The wave packet will dissociate if the laser intensity remains high ($\sim 2 \times 10^{14}$ W/cm^2) when it reaches the (field-free) outer turning point, but it reflects from the outer potential energy surface if the field is low.

Our work is closely related to intense field midinfrared experiments [1], and the related analysis [8,9]. Although the carrier frequency is higher in our experiment, the vibrational wave packet does not respond to the carrier frequency but to the envelope. The envelope period that we use corresponds to infrared frequencies. A great advantage of our (highly multiphoton Raman excitation) method over infrared experiments is that we can change the modulation period easily and continuously.

Our study also bears on coherent control experiments [10,11]. Selective molecular dissociation in neutral or charged molecules [12–14] has been demonstrated using femtosecond optical pulses that have been shaped and frequency chirped by optical phase modulators controlled by genetic algorithms. Although genetic algorithms provide an existence proof for coherent control, in most cases the mechanism of control is not apparent. We provide an understanding of one example of selective molecular dissociation, using a simple molecule and a simple deterministic pulse shape.

To produce the beat wave, we use an OPA pumped by a 500 Hz, 40 fs, 810 nm, 800 μJ Ti:sapphire laser system.
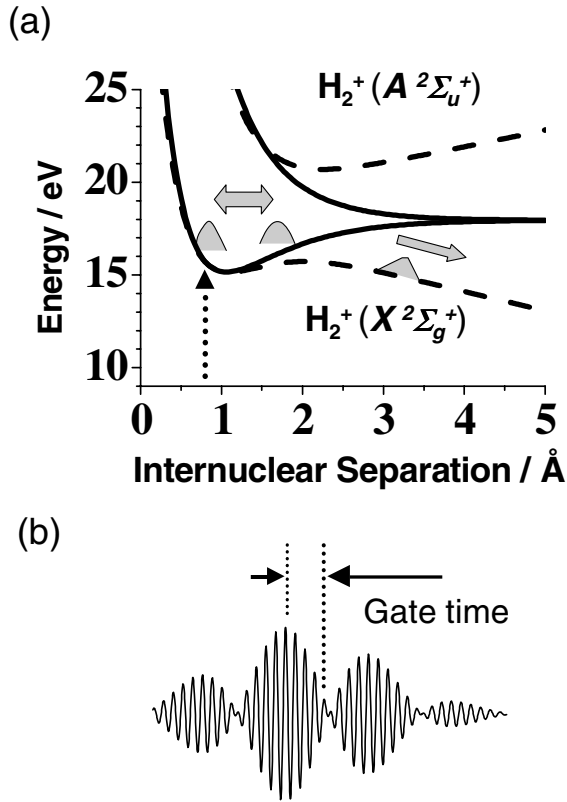
(a)

(b)

FIG. 1. (a) Schematic diagrams for the selected potential energy surface of H_2^+ in field-free (solid) and field-perturbed (dotted) conditions. Tunnel ionization launches the vibrational wave packet on the $H_2^+ X$ surface at the peak of the laser field. The wave packet propagates on the field-distorted X state. When the vibrational wave packet reaches the outer turning point, it will dissociate if the field is on, but will be trapped if the field is off. By tuning the modulation period to the vibrational period of the molecule, we can force it to dissociate or not. Part (b) illustrates the modulated laser field, composed of two fields of different frequencies, and the definition of gate time.

The signal and idler outputs are separated by a polarizer. After being independently delayed, the two beams are recombined at a second polarizer, and pass through a Bereks compensator to create circular polarization. To obtain a linearly polarized beat wave, a third polarizer is used. We obtain 70 fs duration pulses with an optical carrier wavelength of 1.62 μm, modulated with an envelope whose full period varies from 10 to 60 fs, corresponding to signal wavelengths of 1280 to 1550 nm and idler wavelengths of 2200 to 1700 nm. The electric field is given as $E(t) = E_0 \cos(\omega_1 t) + E_0 \cos(\omega_2 t) = E_0 \cos[(\omega_1 + \omega_2)t/2] \cos[(\omega_1 - \omega_2)t/2]$. Here, $\omega_{1,2}$ are the optical angular frequencies of signal and idler. The time between node and antinode is $t_g = \pi/(\omega_1 - \omega_2)$, which we define as the gate time [Fig. 1(b)].

The modulated pulse is then focused in a vacuum chamber using an on-axis parabolic mirror. We estimate the focal spot diameter to be ~ 8 μm. H_2 or D_2 gas is leaked into the vacuum chamber at a pressure of $\sim 10^{-6}$ Torr. A time-of-flight (TOF) mass spectrometer with flight axis perpendicular to the direction of propagation of the laser beam detects H^+ or D^+ fragments, and can measure their kinetic energy. By using a 1 mm hole in the plate of the TOF, only those dissociation fragments that originate from molecules that are aligned within 8° of the TOF axis are observed. The laser pulse is polarized parallel to the TOF axis so we only observe molecules that experience the laser field parallel to the internuclear axis.

We select a peak laser intensity of 2×10^{14} W/cm², verified by ionization of xenon. We confirm that the beams are overlapped both in space and in time inside the chamber by optimizing signal count rate for the fragments.

Figure 2 shows the H^+ signal count as a function of time of flight (lower scale) and corresponding kinetic energy (upper scale). Forward and backward dissociation is responsible for the symmetric peaks of the TOF spectrum [15]. We normalize the signal count by dividing by the H_2^+ signal. The peak at 0.5 eV in Fig. 2 is associated with dissociation due to the laser-induced coupling between the X and the A states, known as bond softening [15]. The peak around ~ 2 eV is due to enhanced ionization by the laser field [16,17]. The square data points correspond to a nonmodulated laser pulse.

The open circles in Fig. 2 show that when we introduce modulation onto the pulse, using a gate time of ~ 8 fs, while keeping the total laser intensity constant, the H^+ count rate is reduced compared with a nonmodulated pulse. This is true for all fragment kinetic energies.
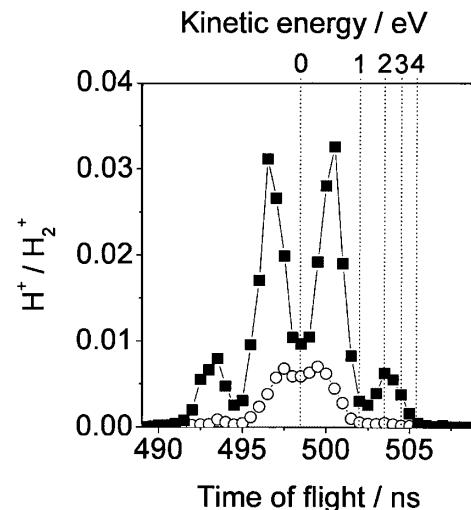

FIG. 2. The time-of-flight H^+ signal from dissociating H_2. The intensity is normalized by the signal of H_2^+. The squares show the signal when the laser field is not modulated. The circles are for a modulated laser pulse ($t_g = 8$ fs). Modulation at this period has the effect of suppressing dissociation.

We show that the difference in the two signals is due to the laser intensity experienced by the wave packet when it reaches the outer turning point. The vibrational wave packet is launched in the molecular ion when one electron is removed near the peak of the laser pulse envelope. This localizes the wave packet at a specific time within the beat wave. If the envelope is still strong at the time that the wave packet reaches its outer turning point (as it is for an unmodulated pulse), the ground state potential energy surface is lowered and dissociation results. On the other hand, if the laser intensity is low at the time at which the wave packet reaches the outer turning point, the field-free potential will reflect the wave packet and few fragments will be observed.

Figure 3(a) is a plot of the integrated signal in the range 0–1.2 eV as a function of the gate time, t_g. The vertical scale is normalized so that the ratio of the signal count of H^+ to its parent ion, H_2^+, is unity when the laser field is

not modulated. The maximum suppression of the dissociation yield for H_2^+ is found at ~8 fs. That time is slightly shorter than the half-period of the H_2^+ vibrational wave packet in field-free conditions, ~9 fs (see below). For comparison, in Fig. 3(b) the dissociation yield of D^+ from D_2^+ is plotted. The gate time which gives the maximum suppression is now ~11 fs. The experimental error bars are contained within the size of squares (circles) in Fig. 3. The difference between H_2^+ and D_2^+ indicates that the modulation period is related to the mass-dependent motion of the vibrational wave packet.

Figure 3 also contains results from a quantum mechanical model. To calculate the motion of the wave packet, we follow three steps. First, we create the initial wave packet by projecting the ground state wave function of H_2 onto the H_2^+ ($X^2\Sigma_g$) state, assuming tunnel ionization. Because the rate of tunnel ionization depends exponentially on the ionization potential, and because the ionization potential decreases with increasing internuclear separation, in addition to the Franck-Condon factors, we must also include the radial dependence of the ionization rate [7,18]. The initial wave packet has contributions from vibrational eigenstates between $v = 0$ and $v = 10$, with $v = 1$ being the most probable. With the initial wave packet established, we calculate the vibrational wave packet motion on the field-modified potential energy surfaces using the time-dependent Schrödinger equation with the split-operator method [19]. It is sufficient to consider only two levels, $X^2\Sigma_g$ and $A^2\Sigma_u$ [20]. These two states are coupled by $\mu E(T)$, where μ is the dipole moment and $E(t)$ is the time-dependent laser field, given by $E(t) = A(t)[\cos(\omega_1 t + \phi) + \cos(\omega_2 t + \phi)]$, where $A(t)$ is a slow envelope function, and ϕ is the carrier envelope phase. When the vibrational wave packet approaches an internuclear separation of ~2.5 Å, nonadiabatic coupling between $X^2\Sigma_g$ and $A^2\Sigma_u$ becomes significant [1], and has the effect of promoting population to $A^2\Sigma_u$. At the end of the propagation time, when the field is off, we classify the wave packet into two parts: We regard the wave packet density inside of 3 Å as trapped, and outside of 3 Å as dissociated.

Since our experiment is not interferometrically stable, we account for fluctuation of the relative phase of the pulses, by changing the value of $\phi/[(\omega_1 + \omega_2)/2]$ in the range -30 to 30 fs centered at the peak of laser envelope. The dissociation yield for each phase was weighted by the initial ionization rate and summed incoherently.

We plot the calculated ratio between dissociated and trapped probabilities as a function of gate time as a solid line in Fig. 3. The agreement between experiment and model confirms our qualitative interpretation. There are no free parameters in the model except the laser intensity. Here we use a laser intensity that is the same as the experimental intensity of 2×10^{14} W/cm². The model shows that there is a well-defined gating time where dissociation is suppressed for all laser intensities. This
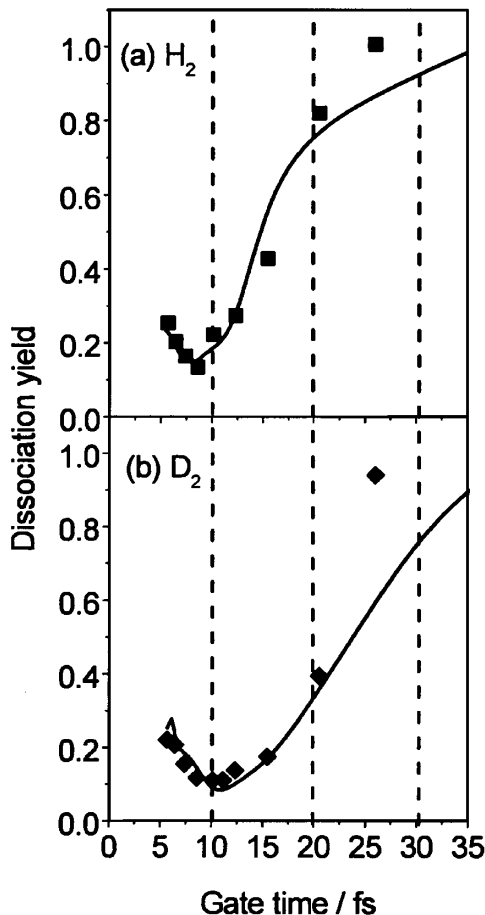
FIG. 3. The dissociation yield curve of (a) H_2^+ and (b) D_2^+ as a function of gate time. The squares are the observed signal counts, normalized to 1 for long gate time. The maximum suppression of the dissociation yield is seen to be ~8 fs for H_2^+ and ~11 fs for D_2^+. The solid lines are from the model described in the text.

time shifts slightly (~ 1 fs) over the intensity range of $(1$–$3) \times 10^{14}$ W/cm^2.

In summary, using a molecule that can be accurately modeled, we show how nonresonant radiation can control dissociation. We have emphasized that a beat wave provides a simple method to achieve this control. Few-cycle pulses, becoming available in a few labs, provide an alternative. It may be possible to produce a precisely timed series of three pulses, each as short as 5 fs in duration and with arbitrary pulse separations. Each of these subpulses could have a well-defined function. The first pulse could launch the vibrational wave packet, the second could guide its path at critical times during the wave packet's evolution, and the third could image the result of the experiment by Coulomb explosion imaging [21]. Other pulses could be added to give even further control, for example over the alignment of the molecule. This route to future experiments would allow us to measure and control small molecules with precision.

Controlling the potential energy surfaces may open the route to selective bond dissociation of large molecules. If vibrational wave packets with different bond frequencies can be produced, then it may be possible to control the dissociation yield by changing the modulation period. The modulation period that we achieve using the OPA is shorter than could be achieved with a pair of even today's shortest optical pulses, and so this may be the best method to excite high-frequency bonds such as CH in larger molecules.

It is not clear at this time whether this method can be extended to larger molecules. However, the understanding that is gained by studying simple molecular systems such as H_2 and D_2 can perhaps shed light on coherent control experiments in larger systems. All molecules have a polarizability through which the laser field can couple to the vibrational motion. Whether this technique will work for larger molecules, with many degrees of freedom, remains to be seen.

[1] P. Dietrich and P. B. Corkum, J. Chem. Phys. **97**, 3187 (1992).

[2] H. Stapelfeldt, H. Sakai, E. Constant, and P. B. Corkum, Phys. Rev. Lett. **79**, 2787 (1997).

[3] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).

[4] J. Karczmarek, J. Wright, P. Corkum, and M. Ivanov, Phys. Rev. Lett. **82**, 3420 (1999).

[5] D. M. Villeneuve *et al.*, Phys. Rev. Lett. **85**, 542 (2000).

[6] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950).

[7] H. Niikura *et al.*, Nature (London) **417**, 917 (2002).

[8] H. A. Rachild, T. T. Nguyen-Dang, R. K. Chaudhury, and X. He, J. Chem. Phys. **97**, 5497 (1992).

[9] F. Châteauneuf, T. T. Nguyen-Dang, N. Ouellet, and O. Atabek, J. Chem. Phys. **108**, 3974 (1998).

[10] P. Brumer and M. Shapiro, Annu. Rev. Phys. Chem. **43**, 257 (1992).

[11] L. Zhu *et al.*, Science **270**, 77 (1995).

[12] R. J. Levis, G. M. Menkir, and H. Rabitz, Science **292**, 709 (2001).

[13] T. Brixner, N. H. Damrauer, P. Niklaus, and G. Gerber, Nature (London) **414**, 57 (2001).

[14] T. C. Weinacht *et al.*, Chem. Phys. Lett. **344**, 333 (2001).

[15] A. Zavriyev, P. H. Bucksbaum, J. Squier, and F. Salin, Phys. Rev. Lett. **70**, 1077 (1993).

[16] T. Seideman, M. Yu. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).

[17] G. N. Gibson, M. Li, C. Guo, and J. Neira, Phys. Rev. Lett. **79**, 2022 (1997).

[18] G. L. Yudin and M. Yu. Ivanov, Phys. Rev. A **63**, 033404 (2001); **64**, 019902 (2001).

[19] A. D. Bandrauk and H. Shen, J. Chem. Phys. **99**, 1185 (1993).

[20] I. Kawata, H. Kono, and Y. Fujimura, J. Chem. Phys. **110**, 11152 (1999).

[21] H. Stapelfeldt, E. Constant, H. Sakai, and P. B. Corkum, Phys. Rev. A **58**, 426 (1998).