# Phase Control in the Two-Color Photodissociation of HD$^+$

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We report on the use of the relative phase between a two-color optical field (1053 and 527 nm) to coherently control the photodissociation of the HD$^+$ molecule. The field-induced spatial asymmetry in the fragment spectrum shows a strong phase dependence, while no selectivity is produced in nearly isoenergetic channels. The positively charged fragments are observed to preferentially dissociate in a direction counterintuitive to classical expectations.

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The possibility of using a *"tailored"* light field to selectively direct reaction pathways (physical or chemical) has been investigated since the advent of coherent light sources. To go beyond the control exercised by varying the frequency of an optical field near an atomic or molecular resonance, which has the obvious limitation of providing little selectivity between allowed transitions to nearly degenerate levels, towards the optimal control [1] of the formation and evolution of an excited atomic or molecular wave function through the coherent properties of the light has become a great experimental challenge. Recent advances in pulse shaping [2], as well as in real-time pulse diagnostics [3], suggest that maximal control of a pulse's amplitude, frequency spectrum, and phase may be realized in the near future. Theoretical models have used such tailored pulses to coherently guide a system through a superposition of many intermediate states to a predetermined output channel [4]. At a less complex level, it has been demonstrated theoretically [5] that the relative phase between two harmonic optical fields is sufficient to coherently control the branching ratios between exit channels in some molecular photodissociation processes. The experimental realization of this has proven to be more difficult, but important steps have been made in photoionization studies. Atomic experiments have demonstrated the modulation of both photoelectron yield (via an interference in a bound-bound transition probability) [6] and angular distribution [7,8] with the relative phase between a two-color optical field. The phase dependence of the photoelectron yield has also been observed in a two-color molecular experiment [9]. In this Letter, we report the first use of the relative phase in a two-color light field to control a photodissociation process. The study shows that photodissociation of a heteronuclear diatom (HD$^+$) results in a sensitive phase dependence of the spatial distribution of ion fragments but no selectivity in the nearly isoenergetic fragment channels.

The molecular hydrogen ion and its isotopic variants (H$_2^+$, D$_2^+$, and HD$^+$) display a very rich structure in their interactions with intense laser pulses. The photodissociation occurs between the bound $1s\sigma$ and repulsive $2p\sigma$ states, which are plotted in Fig. 1. Other levels are much higher in energy ($\approx 11$ eV) and may be neglected in the

present study. A great deal of the interesting behavior from such a seemingly simple system arises from the strong coupling due to the optical field itself. In terms of diabatically dressed molecular states, the field couples the $1s\sigma$ dressed by $n$ photons and the $2p\sigma$ dressed with $m$ photons, where $n$ and $m$ are positive integers and $n - m$ is a positive odd integer. Much of the physics may then be understood in terms of the resulting level repulsion [10]. For example, bond softening [11] arises from the depression of the bound state barrier near a level anticrossing, while above threshold dissociation [10] may be understood in terms of constraints on the system to pass diabatically or adiabatically through particular anticrossings. Vibrational trapping [10] can occur when the potential curves are sufficiently distorted that potential wells deep enough to support bound states form at large internuclear distances. It has been shown theoretically that some selectivity between these competing processes, as well as control over the photofragment angular distribution, can be achieved through the relative phase in a two-color experiment [12,13].

The dynamics is even richer in the heteronuclear case, HD$^+$, as the nuclear mass difference couples the electronic and nuclear motions, lifting the degeneracy of the bound and repulsive states at large internuclear separation by 29.8 cm$^{-1}$ (see inset, Fig. 1). Because of the mixing of
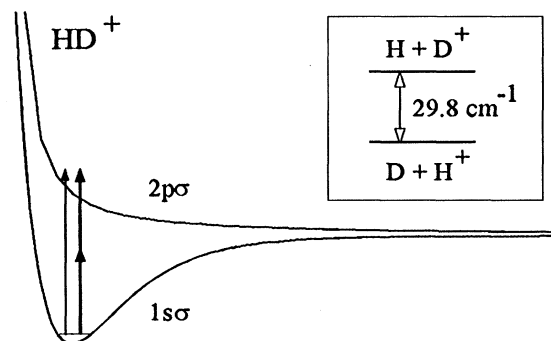


FIG. 1. Potential curves for the $1s\sigma$ and $2p\sigma$ states of HD$^+$. In the homonuclear case, the two states are asymptotically degenerate; the degeneracy is lifted in the heteronuclear case by 29.8 cm$^{-1}$ (inset).

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states of opposite symmetry, both electronic states acquire permanent dipole moments, opposite in sign, which distinguish the two asymptotic dissociation channels $HD^+ + nh\nu \rightarrow H^+ + D$ and $HD^+ + nh\nu \rightarrow D^+ + H$. Electric dipole transitions within the electronic state are then allowed, and it has been shown theoretically [14] that the interference of these intraelectronic and interelectronic couplings can be manipulated through the relative phase of a two-color optical field to *spatially separate* the two dissociation channels. Consequently, the present study has important implications towards the realization of chemical control.

In the experiment reported here, linearly polarized light composed of two wavelengths, 1053 nm and its second harmonic, is first used to photoionize HD through a nonresonant multiphoton process to form $HD^+$ ($HD + mh\nu \rightarrow HD^+ + e^-$), and subsequently dissociate it. The separability of the ionization and dissociation processes for picosecond pulses has been well established in previous one-color studies [10]. The molecule is rapidly rotated into alignment with the polarization axis [15], and the dissociation fragments are preferentially emitted close to this axis. We observe a dramatic asymmetry in the direction of emission of the charged dissociation fragment, controllable through the relative phase, as predicted by Charron, Giusti-Suzor, and Mies [12]. The asymmetry closely follows the asymmetry of the optical electric field, described below, and appears to be the same for both dissociation channels; a phase-dependent asymmetry in the spatially resolved branching ratio, which is predicted to be large at longer wavelengths [14], is not observed in this experiment.

The time dependence of a linearly polarized optical field composed of two frequencies, a fundamental $\omega$ and its second harmonic $2\omega$, with respective electric field amplitudes $E_1$ and $E_2$, as a function of the relative phase $\phi$ is given by

$$E = E_1 \cos(\omega t) + E_2 \cos(2\omega t + \phi). \tag{1}$$

The extrema of this field have different magnitudes in the forward (positive) and backward (negative) directions, and the size of this asymmetry is a function of the relative phase. It is largest at $\phi = 0$, with the maximum being larger in the forward direction, and again at $\phi = \pi$, where the maximum is larger in the backward direction. The wave form is illustrated for several values of $\phi$ in Fig. 2. The magnitude of the field maximum without respect to direction has a periodicity of $\pi$ in the relative phase, while the periodicity of the maximum field in either direction is $2\pi$. In free space, the spatial frequencies of the two-color components are in the same proportion as their temporal frequencies, and the relative phase does not change along the propagation direction, except through a focus. In a dispersive medium, this is no longer true, and the phase may be varied by simply changing the length of dispersive material traversed by the beam.
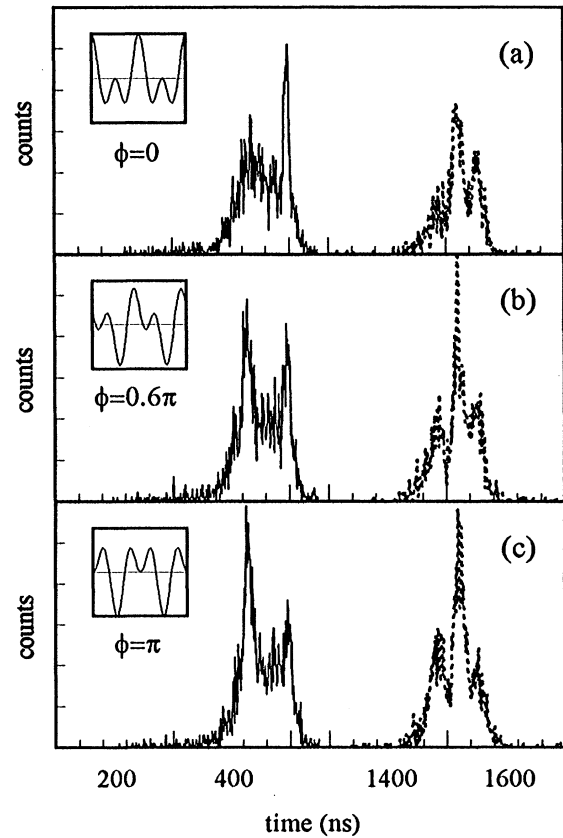


FIG. 2. Time-of-flight spectra expanded about the $H^+$ (solid) and $D^+$ (dashed) arrival peaks for (a) $\phi = 0$, (b) $\phi = 0.6\pi$, and (c) $\phi = \pi$. The optical electric field [$E_1 = E_2$ in Eq. (1)] is plotted over two optical cycles in the inset of each graph for the corresponding value of the two-color relative phase $\phi$. The dissociation fraction is 0.12. The total intensity is $2 \times 10^{13}$ W/cm$^2$.

The 1053 nm fundamental is produced in 50 psec pulses in a mode-locked Nd:YLF laser and amplified in a regenerative amplifier to 2 mJ at a 1 kHz repetition rate [16]. After passing through a variable attenuator, the light is doubled in a $\beta$-barium borate crystal. A wave plate which provides half and full wave retardance for the infrared and green light, respectively, permits rotation of the infrared polarization, leaving the green polarization unchanged. This, in conjunction with a polarizer further in the beam path, allows selective attenuation of the infrared component of the beam. A 5 mm thick glass plate on a rotation stage is used to vary the relative phase between the green and infrared light. The optical path lengths for the two colors change at different rates with the angle of the plate, due to dispersion. A Glan-Taylor polarizer functions as part of the infrared attenuator and to assure the purity of the linearly polarized light. The light is focused with $f/5$ optics to a maximum total intensity of approximately $2 \times 10^{13}$ W/cm$^2$, at the focus of a pair of time-of-flight spectrometers, one for electrons

and one for ions, located in an ultrahigh vacuum chamber (ultimate pressure $3 \times 10^{-10}$ torr). The light polarization is parallel to the spectrometer axis. HD gas is leaked into the chamber to pressures of $5 \times 10^{-6}$ to $4 \times 10^{-5}$ torr, the count rate being limited to 0.5 count/shot, 2 orders of magnitude below the rate at which space charge begins to affect the energy spectrum. An extraction field is applied along the spectrometer axis during ion detection to distinguish ions with initial velocities in the forward (toward the detector) and backward (away from the detector) directions. The latter are turned around in the extraction field and have longer flight times than the former. Consequently, the arrival time difference between the forward and backward components is a direct measure of the fragments' initial kinetic energy.

The phase between the green and infrared components is calibrated by replacing the HD sample gas with krypton and examining the photoelectron energy spectrum, following the work of Schumacher *et al.* [8]. The krypton calibration for photoelectrons emitted towards the detector as a function of phase is shown in Fig. 3(c). The periodicity
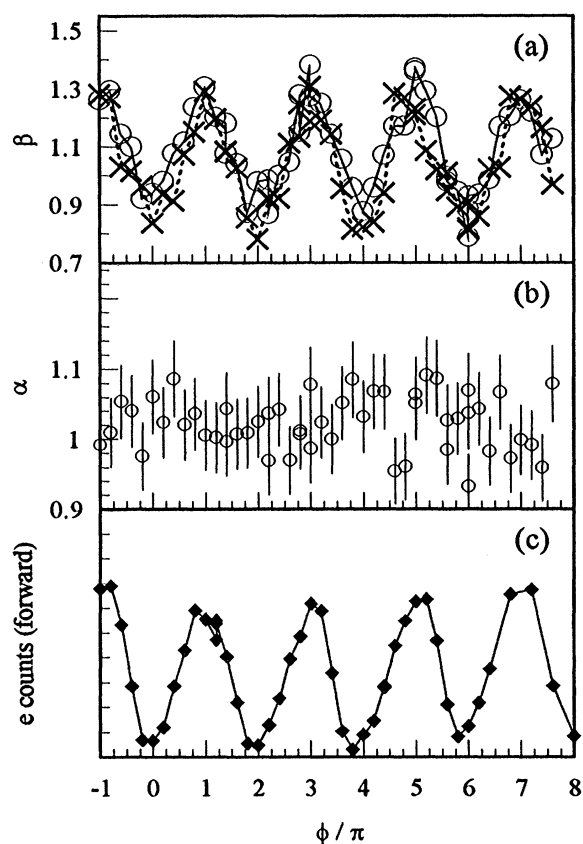


FIG. 3. (a) The forward/backward yield ratios $\beta_{H^+} = H_f^+/H_b^+$ (circles) and $\beta_{D^+} = D_f^+/D_b^+$ (crosses) of protons and deuterons vs the relative two-color phase $\phi$ in the dissociation of HD$^+$. (b) Plot of isotope separation, $\alpha$, vs $\phi$ (see text for details). The uncertainty is indicated by the error bars. (c) Krypton photoelectron yield towards the detector vs $\phi$.

of the phase adjustment plate was also checked by adding a second doubling crystal after the plate and measuring the interference between the second harmonic produced in the first and second doubling crystals [17] as a function of the phase adjustment plate angle.

Typical time-of-flight spectra, expanded about the H$^+$ and D$^+$ peaks, are shown in Fig. 2 for phases of 0, $0.6\pi$, and $\pi$. The arrival time spectrum reflects the kinetic energy spectrum of the ions at the time of dissociation, the later peak representing those ions that originated with a velocity in the "backward" (away from the detector) direction. The D$^+$ spectrum has an additional center peak due to contaminant H$_2$ (2% of the sample gas) which is photoionized to form H$_2^+$ with a thermal velocity distribution. The energy at the peak of the distribution is 0.5 eV, indicating that the dissociation process is predominantly bond softening. Above threshold dissociation accounts for less than 5% of the dissociation yield. Ions of both species are preferentially emitted *away* from the detector at $\phi = 0$, when the optical electric field maximum points *toward* the detector [Fig. 2(a)]. Conversely they are emitted preferentially toward the detector at $\phi = \pi$, when the field maximum points away from the detector. Obviously, symmetric field distributions ($\phi = \pi/2$) yield symmetric ion distributions.

The ratios of forward to backward yields for each isotope, $\beta_{H^+}$ and $\beta_{D^+}$, are plotted in Fig. 3(a) over several cycles. There is a clear periodicity of $2\pi$ in the relative phase, following the modulation in the asymmetry of the optical electric field. We observe that the yield of the molecular ion, HD$^+$, also oscillates with the relative phase, with a period of $\pi$, following the modulation of the absolute magnitude of the optical electric field maximum. However, this modulation in the size of the HD$^+$ source for the photodissociation, which can be as large as 25%, cancels out in the ratios $\beta_{H^+}$ and $\beta_{D^+}$. Any phase-dependent modulations in the vibrational state distribution of the molecular ion, which are not monitored in the experiment, could affect the magnitude of the modulation in $\beta_{H^+,D^+}$, but cannot in themselves give rise to the modulation.

Figure 4 shows the depth of modulation as a function of the fraction of the green to the total intensity, $I_{2\omega}/(I_\omega + I_{2\omega})$, for deuterons. The largest modulation occurs for nearly equal intensities of green and infrared, for which the largest modulation in the maximum of the optical electric field also occurs. The same modulation, with the same phase, was observed in the dissociation of H$_2^+$. Considering that the experiment averages over the spatial and temporal intensity distribution of the laser pulse and the initial vibrational state distribution, the depth of modulation is surprisingly robust.

The close overlap of $\beta_{H^+}$ and $\beta_{D^+}$ curves in Fig. 2(a) indicates that there is no phase-dependent directional isotope separation. Such a separation, i.e., a phase-dependent variation in the yield ratio $\alpha \equiv H^+/D^+$ in either the forward or backward direction, has been predicted for
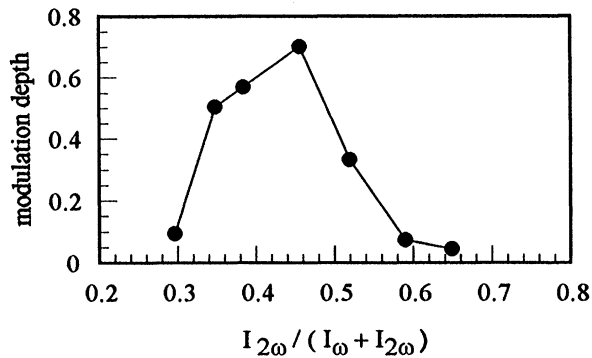
FIG. 4. Modulation depth of the $\beta_{D^+}$ (deuterons) vs $\phi$ as a function of the green fraction of the light intensity. The curve is similar for protons. The total intensity is $\approx 2 \times 10^{13}$ W/cm$^2$.

a two-color field composed of longer wavelengths [13]. Experimentally, the direct measure of $\alpha$ is complicated by the unknown mass dependence of the microchannel plate detector efficiency. This can be eliminated by analyzing the ratio of the two $\beta$ ratios plotted in Fig. 3(a), in terms of $\alpha^2 = H_f^+ D_b^+ / D_f^+ H_b^+ = \beta_{H^+}/\beta_{D^+}$, where the $f$, $b$ subscripts indicate the yield in the forward and backward directions, respectively. The resulting $\alpha$ ratio is plotted in Fig. 3(b) as a function of phase and clearly shows that there is no phase-dependent isotopic separation within an uncertainty of 9%.

The periodicity of the forward/backward ratio, $\beta$, is equal to that of the maximum instantaneous field in one direction, but surprisingly, as mentioned above, the positively charged fragments are emitted preferentially in the direction *opposite* that in which the field maximum points. To illustrate this point, Fig. 3(c) plots the electrons emitted towards the detector as a function of phase for the photoionization of krypton atoms. This observation is consistent with a classical interpretation, where the electron accelerates down field (opposite field maximum). Extrapolating this behavior for photodissociation of HD$^+$, one might expect that as the fragments moved apart, the electron would tend down field, forming the neutral product (H or D), while the positively charged fragment heads up field. However, comparison of Figs. 3(a) and 3(c) clearly shows that this is not the case; the positively charged photofragments are preferentially emitted in the same direction (in phase) as the Kr photoelectrons, contrary to simple classical expectations. Furthermore, there is no deviation from this behavior for the intensity range (Fig. 4) investigated in this study.

In conclusion, we have used the relative phase between the two composite colors of an optical field to modulate the fragment distribution in the photodissociation of HD$^+$. While there appears to be no significant phase-dependent selection of the molecular potential curve along which the photodissociation of the ion occurs, there is some selection of the exit channel in the form of a dramatic modulation in the angular distribution

of the photodissociation fragments. The period of this modulation is equal to the modulation period of the asymmetry of the composite optical electric field, but the direction in which the charged fragment exits is opposite to that which one would expect in a naive classical picture. A partial resolution to this contradiction could lie in the small parameter space probed in the experiment but no unambiguous interpretation of this effect currently exists. Thus, further experimental and theoretical treatment is warranted.

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