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Selective photodissociation of O–H and O–D bonds from ground vibrational state of HOD using simple UV pulses

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Selective cleaving of both O–H and O–D bonds in HOD is achieved using reasonably simple UV pulses to excite the HOD molecule in its ground vibrational state to the repulsive first excited \( \tilde{A} (\tilde{1} B_1) \) surface. Detailed theoretical analysis of population transfer and flux in the H+O–D/H–O+D channels reveals an important preparatory role for the cross-talk between the participating levels and a possible role for the beat structure of the population transfer oscillations in facilitating selective dissociation. Excitation using a 50 fs single color 67 169 cm\(^{-1}\) laser pulse achieves a branching ratio H+O–D/H–O+D=5.64 with 82\% flux in the H+O–D channel and 15\% in the H–O+D channel. A two color 50 fs laser pulse with frequencies of 54 920 and 52 303 cm\(^{-1}\) provides a branching ratio of H–O+D/H+O–D=2.83 and 52\% flux in the H–O+D channel and 18\% in the H+O–D channel. © 2007 American Institute of Physics.

I. INTRODUCTION

Selective control of bond breaking is a dream of enduring interest,\(^1\)\^2\^-\(^6\) and HOD where the O–H and O–D bonds can be separately excited has served as a popular prototype for experimental and theoretical tests of many ideas.\(^7\)\^-\(^30\) The first excited state \( \tilde{A} (\tilde{1} B_1) \) of HOD being totally repulsive, most approaches to selective control of O–H and O–D dissociations have been based on selective population transfer to H+O–D/H–O+D region of the \( \tilde{A} (\tilde{1} B_1) \) surface. Based on the demonstrated separability of the bending mode from the stretching modes\(^31\)\^-\(^32\) and absence of a bending progression in the Raman spectrum,\(^33\)\^-\(^\infty\) most approaches to selective dissociation of O–H and O–D bonds have been two dimensional (2D) with the bending angle frozen at the equilibrium bond angle. Although considerable selectivity in dissociation of the O–H bond has been demonstrated without prior vibrational excitation of the O–H bond,\(^8\)\^-\(^12\)\^-\(^20\)\^-\(^26\)\^-\(^30\) in most cases, prior excitation\(^8\^-\(^18\)\^-\(^22\)\^-\(^25\) of the O–H bond to ensure its deposition in the H+O–D channel on transition to the repulsive \( \tilde{A} (\tilde{1} B_1) \) surface has been the more favored route. In the case of selective dissociation of the O–D bond via transition to the repulsive first excited surface, prior excitation in the O–D stretch has been necessary.\(^1\)

The second excited \( \tilde{B} (\tilde{1} A_1) \) surface is much more anisotropic with a potential minimum at the linear configuration which is significantly displaced vis-a-vis the minimum in the ground surface. Excitation to this surface, therefore, immediately opens the bending angle\(^34\)\^-\(^35\) under the influence of a strong torque, and a full three dimensional (3D) treatment including the bending mode becomes necessary. In the control scenarios mediated via the \( \tilde{B} (\tilde{1} A_1) \) surface, both artificial channel based 3D scattering calculations\(^1\) which achieve selectivity by inhibiting the dissociation of one bond while leaving the other unchanged and a two pulse coherent radiative control\(^1\) where a prior superposition of excited vibrational states on the ground surface is subjected to a vacuum ultraviolet pulse taking it to dissociative continuum of the \( \tilde{B} (\tilde{1} A_1) \) surface have shown an excellent selectivity in preferential dissociation of both the O–H and the O–D bonds.

Since the \( \tilde{A} (\tilde{1} B_1) \) surface mediated 2D treatments are computationally less demanding and have demonstrated a desired selectivity in the preferential dissociation of O–H/O–D bonds, we have followed the 2D route to the selective control of HOD photodissociation mediated by the first excited surface. We offer new scenarios which provide a selectivity with large yield for dissociation of any of the two O–H/O–D bonds using simple UV pulses with an important role for the cross-talk between the ground and the excited surfaces. The results to be presented do not require a prior vibrational excitation of the O–H or the O–D bond and improve upon earlier attempts involving the solution of two surface time dependent Schrödinger equation\(^18\^-\(^20\^-\(^25\) by using pulse shapes which have a sufficiently narrow frequency bandwidth to ensure that the mechanistic analysis based on excitation of individual vibrational levels remains feasible.

The following section presents an outline of computa-
tional considerations and is followed by a discussion of results. A summary of main observations concludes this paper.

II. METHOD

The first and second excited potential energy surfaces of HOD are well separated and following an earlier work, we too have considered only the ground and the first excited potential energy surfaces with bending motion frozen at equilibrium bond angle (104.52°). For femtosecond pulses to be considered here, the rotational motion has been neglected. The time evolution of the nuclear motion of the HOD molecule is then governed by

$$i\hbar \frac{\partial}{\partial t} \langle \Psi_e \rangle = \left( \hat{H}_e + \hat{H}_{uv}(t) \right) \langle \Psi_e \rangle,$$

where $\Psi_e = \Psi_e(r_1, r_2, t)$ and $\Psi_e = \Psi_e(r_1, r_2, t)$ are the ground and excited state wave functions where $r_1$ and $r_2$ refer to O–H and O–D coordinates. The nuclear Hamiltonians for these two electronic states are expressed as $\hat{H}_e = \hat{T} + \hat{V}_e$ and $\hat{H}_e = \hat{T} + \hat{V}_e$ in which $\hat{T}$ and $\hat{H}_{uv}$ are detailed elsewhere. The $\hat{V}_e$ and $\hat{V}_e$ are obtained from Refs. 10, 31, 36, and 37, and Eq. (1) is solved using $\Psi_e$ as ground vibrational state of the HOD and $\Psi_e = 0$, at $t = 0$.

The vibrational eigenfunctions of HOD have been obtained from two dimensional Fourier grid Hamiltonian method. In the time propagation of wave functions $\Psi_e(t)$ and $\Psi_e(t)$, the effect of kinetic energy operator on the wave function is evaluated using a two dimensional fast Fourier transform, and the Lanczos scheme has been used for time propagation. We have used a spatial grid spanning $r_{O-H}/r_{O-D}$ bond lengths between 1$a_0$ and 10$a_0$ discretized on a mesh with 128 grid points. As in our previous investigations, we have used the Gaussian UV pulse of the form $E(t) = a(t) \cos \omega t$, where $a(t) = \exp[-(t-t_{uv})^2]$ with full width at half maximum (FWHM) = $\sqrt{2 \ln 2} / \gamma$ and $\Delta t = 1$ a.u. of time $t = 0.0242$ fs. We have used both single and two color laser fields with corresponding maximum field amplitude being 0.46 GV/cm corresponding to the field intensity of 178 TW/cm$^2$.

The time integrated total flux in the competing channels, H+O–D (H–O–D→H+O–D) and H–O+D (H–O–D→H–O+D) are given by

$$J_{H+O-D} = \int_0^{T_{uv}} \int_0^T \psi^*(r_1, r_2, t) \left( j_1 + \mu_2 \cos \theta \right) m_o \sin \theta r_2 dt$$

and

$$J_{H-O+D} = \int_0^{T_{uv}} \int_0^T \psi^*(r_1, r_2, t) \left( j_2 + \mu_1 \cos \theta \right) m_o \sin \theta r_2 dt,$$

where $j_1$ is the flux operator in the $i$th channel, defined as $j_1 = (1/2 \mu_j) [\hat{p}_j \delta(r_i - r_i^d) + \delta(r_i - r_i^d) \hat{p}_j]$, and $\mu_i$, $\hat{p}_i$, and $r_i^d$ are the reduced mass, the momentum operator, and a grid point in the asymptotic region of the $i$th channel, respectively. The ground vibrational state of the molecule is our initial condition and the fluxes in H+O–D/H–O+D channels are evaluated along asymptotic cuts at $r_{O-H} = r_{O-D} = 7.5a_0$. An absorbing optical potential is used to avoid an unphysical reflection from the edges.

III. RESULTS AND DISCUSSIONS

In an earlier investigation, we have mapped the frequency dependence of the photodissociation profile of HOD using single color Gaussian UV pulses of the type shown in Fig. 1(a) for three different initial states $|0,0\rangle$, $|0,1\rangle$, and $|0,2\rangle$, where $|m,n\rangle$ represents $m$ quanta of excitation in the O–H mode and $n$ quanta of excitation in the O–D mode. Our investigations with ground vibrational state $|0,0\rangle$ of the ground electronic state of HOD in the first absorption band showed that the dissociation of O–H bond is favored over O–D bond dissociation in a fairly large band of UV frequencies.

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Fig. 1(b) we have plotted fluxes in both H+O–D and H–O+D channels along with ground and excited state populations for the field profile presented in Fig. 1(a) with the carrier frequency of 67 169 cm$^{-1}$ being the one identified earlier$^{29}$ to provide a maximum H+O–D yield. As can be seen from Fig. 1(b), unlike the one way of ground to excited state transfer pattern assumed in the time dependent wave packet based approaches utilizing idealized $\delta$-function-type pulses,$^{9,10,12,18,26}$ the ground and excited population transfers follow a synchronized pattern, which builds up quickly as the field gains its full strength, and the cross-talk disappears only when the field is switched off at 150 fs providing a kick in the H+O–D flux. For this simple field, there is an $\sim$82% flux in the H+O–D channel as compared to $\sim$15% flux in the H–O+D channel.

Time evolution plots of probability density on both ground and excited surfaces are offered in Fig. 2 for mechanistic insights. In the ground electronic state, the wave function profile of $|0,0\rangle$ does not change, but there is a considerable variation in spatial displacement pattern as the field gains strength at 75 fs, and corner cutting by the probability density in the H+O–D valley of the excited surface leading to a highly oscillating structure in the H–O+D valley is a clear pointer to the field induced changes which may be tapped for selective control. The field induced displacement of the wave function in the ground state pushes the probability density flow in the excited state into the H+O–D channel with a marked enhancement at 75 and 150 fs. At 75 fs, the field starts impacting the molecule in a more pronounced manner, whereas at 150 fs the field effect ebbs and the amplitude remaining in the excited state flows through the H+O–D channel with a sharp pickup in the H+O–D flux, as seen from flux versus time plot of Fig. 1(b). The cross-talk between the two surfaces seems to have an important preparatory role, and the beat structure ($7072 \text{ cm}^{-1}$) of population transfer oscillations [inset of Fig. 1(b)] closely equals the vibrational frequency of the $|2,0\rangle$ state ($7250 \text{ cm}^{-1}$). As a result, the HOD molecule in resonance with this beat frequency may be mimicking the O–H bond oscillations with two quanta of excitation inducing a more favorable dissociation of O–H bond as observed.

Our earlier investigations$^{29,30}$ have shown that single color pulses cannot preferentially dissociate the O–D bond from ground vibrational state, and prior excitation of the O–D bond is required for its selective dissociation. We have shown elsewhere$^{41}$ that mixing of states may be replaced by mixing of colors, and we have therefore extended our approach to examine if two color lasers may be used for preferential dissociation of the O–D bond.

The two color field employed for selective dissociation of the O–D bond and its power spectrum are shown in Fig. 3(a). The beat structure of the resulting pulse displays a frequency of 2752 cm$^{-1}$, which resonates with vibrational frequency of the $|0,1\rangle$ state with one quantum of excitation in the O–D mode ($2727 \text{ cm}^{-1}$) and is also a near multiple of the vibrational frequency for the $|0,2\rangle$ state ($5369 \text{ cm}^{-1}$). Moreover, the combination UV frequency of this 50 fs two color pulse is $\sim55 160 \text{ cm}^{-1}$ [lower inset of Fig. 3(a)], which is very close to the resonance frequency for population transfer from the $|0,2\rangle$ state on the ground surface to the excited electronic state. From this choice of the two color laser pulse, we would, therefore, expect a dissociation pattern for H–O–D characteristic of H–O–D with excited vibration in O–D bond which has been shown to favor O–D dissociation$^{29,30}$ and, as can be seen from the flux versus time plot of Fig. 3(b), the final flux in the H–O+D channel is

FIG. 2. Time evolution of $|0,0\rangle$ state on ground and excited surfaces at $t = 50$, 75, 100, 125, and 150 fs for the field profile shown in Fig. 1(a).
indeed thrice as large as that in the H+O–D channel. The kinematic bias favoring the dissociation of O–H bond can therefore be reversed from ground vibrational state of ground electronic state of HOD with a suitably chosen two color UV pulse.

To garner a mechanistic insight, some snapshots of time evolution from \( |0,0\rangle \) vibrational state of the ground electronic state on both ground and excited surfaces at 50, 75, 100, 125, and 150 fs for the two color laser pulse discussed above are provided in Fig. 4. The cross-talk characterizing the population transfer between the ground and excited surfaces is quite intense [Figs. 3(b) and 4], and the initial \(|0,0\rangle\) probability density profile on the ground electronic state (Fig. 4) undergoes considerable distortions in the 100–150 fs interval, and the nodal topology of the \(|0,0\rangle\) state begins to change from 100 fs onwards. The change of this nodal topology indicates an active manipulation by the two color laser field employed here, and with two nodes clearly visible at 125 fs in Fig. 4 it seems that excited local O–D modes are being prepared by the two color laser field, since at 125 fs, the probability density in ground state is like that of the \(|0,2\rangle\) state.

The field induced synchronized population transfer between the ground and excited surfaces seen in Fig. 3(b) and its correlation with the pulse profile are similar to that discussed for Fig. 1(b) earlier. The time evolution plots on ex-
cited surface at 50–75 fs (Fig. 4) show a simple transfer of probability amplitudes from the ground surface. The flow of probability density into competing channels starts well after the field has peaked, i.e., from 100 fs with the buildup in $H-O+D$ channel starting only after 140 fs when the field intensity is low enough to interrupt the pronounced population exchange, and the flushing of populations can proceed with a small kick in $H-O+D$ flux at 155 fs as expected. Initially (100 fs) the flow of amplitude is towards the $O+H-O$ channel which is altered from 125 fs onwards, and this alteration in the flow of probability amplitude continues until the end of the dissociation process. The final flux in the $H-O+D$ channel (~52%) is approximately three times that of the flux in the $H+O-D$ channel (~18%).

IV. CONCLUDING REMARKS

In conclusion, selective photodissociation in HOD has been shown to be achievable without any need for prior excitation of $O-H$ or $O-D$ bond using a single color laser for preferential dissociation of the $O-H$ bond and a two color laser for the $O-D$ bond. For single color, the dissociation of $O-H$ bond predominates over $O-D$ bond. The probability density flow on the excited surface for this single color pulse provides a quantal analog of corner cutting classical trajectories. The use of an appropriately chosen two color laser pulse reverses the kinematic bias in favor of $O-H$ dissociation, and a preferential dissociation of the $O-D$ bond is observed. The field induced cross-talk between the ground and excited surfaces is seen to facilitate the spatial steering of the probability density on the ground surface, and the resulting beat structure of population transfer oscillations seems to assist in selective control. A more detailed investigation of HOD photodissociation is underway.

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