Chapter 16

Molecular Restructuring in Intense IR Laser Fields

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In an Infra-red (IR) laser field, synchronizing molecular wavepacket motions and the field oscillations can give interesting dynamical effects, suggesting new control schemes. We demonstrate that these effects are intrinsically due to a local time-asymmetry in the time-dependent molecular structure and force field impressed by the laser field on the molecule. We then show how this time-dependent molecular restructuring can be described generally by a simple LCAO scheme involving field-shifted atomic orbitals and show that a laser-induced time-asymmetric force-field is obtained for the water molecule prealigned and strongly driven by an intense IR laser pulse.

In an IR laser field, the nuclear dynamics within a molecule can be synchronized with the laser oscillations to produce effects that are reminiscent of a control scenario. This observation has been illustrated in a series of papers[1],[2],[3] where we showed how the dissociation of diatomic molecules, ranging from the simplest one, the H_2^+ molecular ion to a heavy, many electron molecule, such as HCl^+, can be either quenched or facilitated by synchronizing properly the birth of the initial nuclear wavepacket with the start of the laser's electric field oscillations. In the review to be found in

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the next section, we will show that this dynamical dissociation quenching, DDQ, effect is a reflection of a local time-asymmetry in the laser-induced time-dependent molecular force-field. This in turn reflects the molecular restructuring in the IR field, a result of the strong radiative interactions that also operates in complex molecules. In this sense, it is expected that effects similar to the DDQ effect in diatomic should also exist in polyatomic molecules and could be exploited in time-resolved control schemes involving energy flows among their many internal degrees of freedom.

Molecular restructuring, embodied in the changes in the MO structure induced by a IR laser field, has so far been analyzed in terms of laser-induced interactions between the field-free MOs[4]. A complementary and equivalent view of the molecular orbital restructuring process exists and may prove useful and more insightful when applied to polyatomic molecules. In this view, one considers that the MOs formed in the presence of the field result from the interaction of atomic orbitals (AO) of the constituent atoms already conditioned and shifted by the field. We will outline the principle of the new LCAO scheme, called LCfiAO scheme, using these field-shifted AOs in section 3, and show how the MO structure of H_2O is predicted to change under the action of a IR laser field polarized linearly along the C_2 symmetry axis of the molecule.

Time-asymmetric force field for molecular motions in an IR laser pulse.

The laser-induced Dynamical Dissociation Quenching (DDQ) effect described in our previous work[1]-[3] hinges on how the wavepacket in a diatomic molecular ion, such as H_2^+, HD^+, HCl^+, present themselves with respect to the time-dependent potential barrier to dissociation that the laser field is impressing upon the molecular force field. Let us concentrate for the moment on the H_2^+ molecule. We considered[1] wavepackets launched, on the ground state PES of the molecular ion, at time $t = 0$ of the field oscillations described by an electric-field function of the form $\vec{E}(t) = \varepsilon(t) \cdot \cos(\omega_L t - \delta)$, where $\varepsilon(t)$ denotes a quasi-rectangular pulse shape of amplitude $E_0 (\propto \sqrt{I})$, so that the situation with $\delta = 0$ corresponds to the initial wavepacket being prepared, by vertical promotion from the parent neutral molecule ground state for instance, while the field is at its maximum intensity. In contrast, for $\delta = \pi/2$, the initial state preparation occurs at the start of an optical cycle, i.e. at zero field intensity. The dynamical difference between these two situations resides basically in the timing of the arrival of the wavepacket in the so-called gap region, where the adiabatic potentials W_+ and W_-, defined by diagonalizing the instantaneous

potential matrix $\hat{\underline{W}}(R,t)$:

$$W_{ij}(R,t) = V_i(R)\delta_{ij} - \mu_{ij}(R).\varepsilon(t).\cos(\omega_L t - \delta) \qquad (1)$$

i.e.

$$\underline{C}(R,,t)\hat{\underline{W}}(R,t)\underline{C}^{-1}(R,t) = \begin{pmatrix} W_-(R,t) & 0 \\ 0 & W_+(R,t) \end{pmatrix} \qquad (2)$$

are closest to each other and where a time-dependent barrier is exhibited on the lower potential W_-, Figure 1(a). Arrival at a receding barrier, i.e. closing gap, tends to prevent escape toward the asymptotic region; this leads to the dynamical dissociation quenching (DDQ) effect. Wavepacket arrival at an incoming barrier, or opening gap, permits the escape of an important part of this wavepacket towards the asymptotic, dissociative limit. This is the barrier lowering (and/or suppression) mechanism. In the more general case of the heteronuclear ion HD^+, the presence of a permanent dipole moment introduces an asymmetry in the adiabatic potentials W_+'s temporal dependence[4]. Thanks to this temporal asymmetry, the DDQ effect can, in this case, distinguish even the $\delta = 0$ and π cases, corresponding to different initial orientations of this molecule [2]. Figure 1(b) illustrates the dynamical effect of this asymmetry through a simple classical 'ballistic' model in which we imagine a particle launched at time $t = 0$ towards the gap region, and would exit this region only if its energy exceeds the barrier height encountered there, otherwise the particle is reflected back towards the repulsive wall from where it started. The figure shows the position of the potential barrier as a function of time along with the trajectory of the ballistic particle. The distinction between the cases $\delta = \pi$ and $\delta = 0$ is clearly seen in this simple picture. Figure 1(c) shows how the wavepacket simulation results support this interpretation. On the left panel, we reproduce the curves representing the time evolution of the total bound state population $P_{bound}(t) = \sum_v | < v|\psi(t) > |^2$ as obtained for HD^+ prepared at time $t = 0$ in a field of frequency $\omega_L = 1680 \; cm^{-1}$, of intensity $I = 5 \times 10^{13} \; W/cm^2$ and of varying absolute phase δ. This is to be compared with the results for H_2^+ obtained in the same conditions (but for $\omega_L = 943 \; cm^{-1}$).

That the DDQ effect in diatomic is in fact an effect of the time-asymmetry in the time-dependent force field can further be verified by considering the dynamics of the homonuclear HD^+ molecule in a two-color $(\omega + 2\omega)$ field of the form[5]

$$E(t) = \varepsilon(t).[\cos(\omega_L t - \delta) + 0.5\cos(2\omega_L t - 2\delta + \phi)] \qquad (3)$$

Figure 2(a) illustrates how the combined two-color electric field oscillates in time for various values of the relative phase ϕ between the two waves,
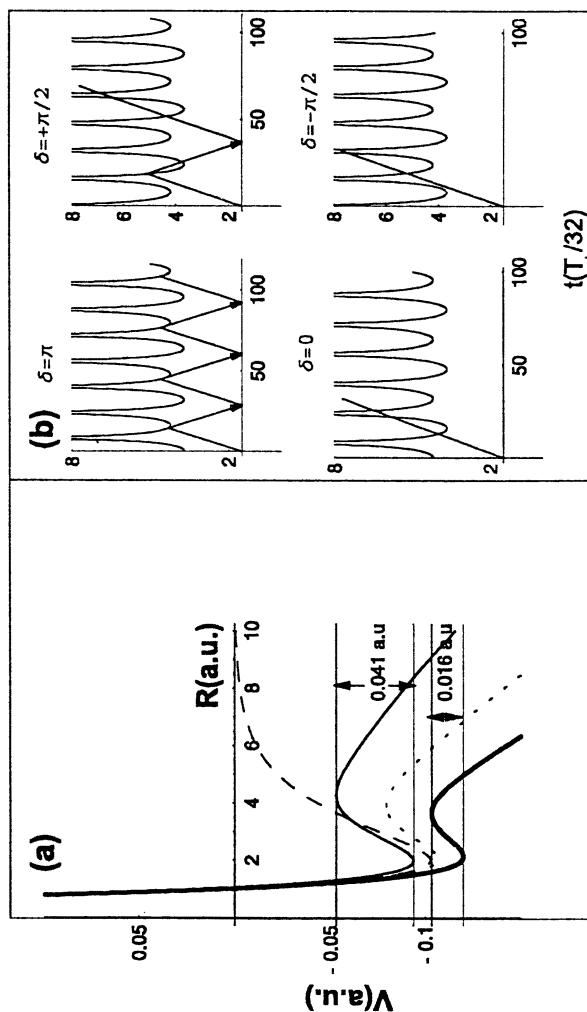
Figure 1(a): Time-dependent ground state potential energy curve W_- for HD^+ when its dipole moment is parallel to $\vec{E}$ (thin solid line), antiparallel to $\vec{E}$ (thick solid line) as compared to the situation in H_2^+ (dotted line) and to the field free potential (dashed line). The field intensity is $I = 5 \times 10^{13}$ W/cm^2.

Figure 1(b): Straight-line trajectory of a ballistic particle (modeling HD^+), launched at time $t = 0$, in a field $\vec{E}(t) = E_0 cos(\omega_L t - \delta)$, $\delta = 0, \pi, +\pi/2, -\pi/2$, towards the moving barrier.
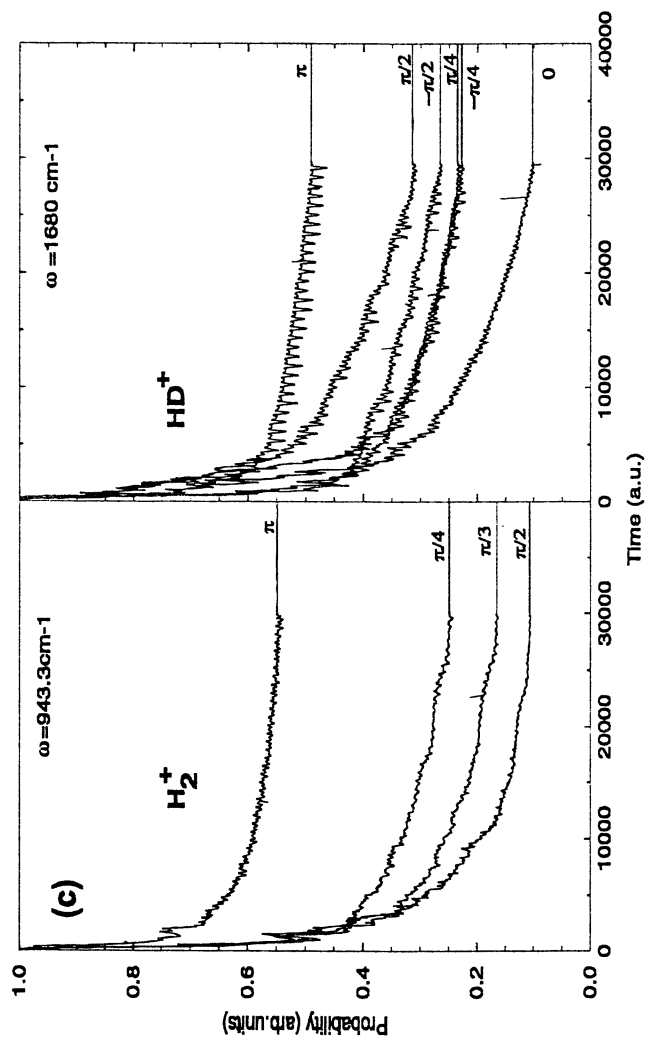
Figure 1(c): Time evolution of P_{bound} for HD^+ (right panel) and H_2^+ in an IR, $I = 5 \times 10^{13}$ W/cm² field of varying absolute phase. The values of the field frequency ω_L and absolute phase are indicated explicitly.
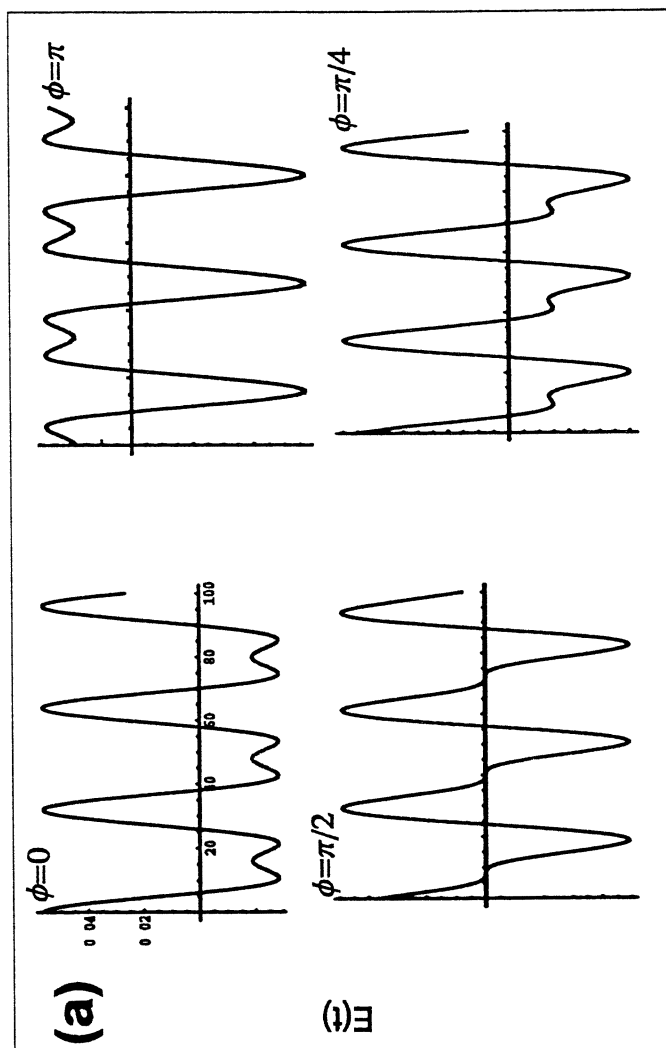
Figure 2(a): *Time-variation of a field of the form given in eq.(3), with*
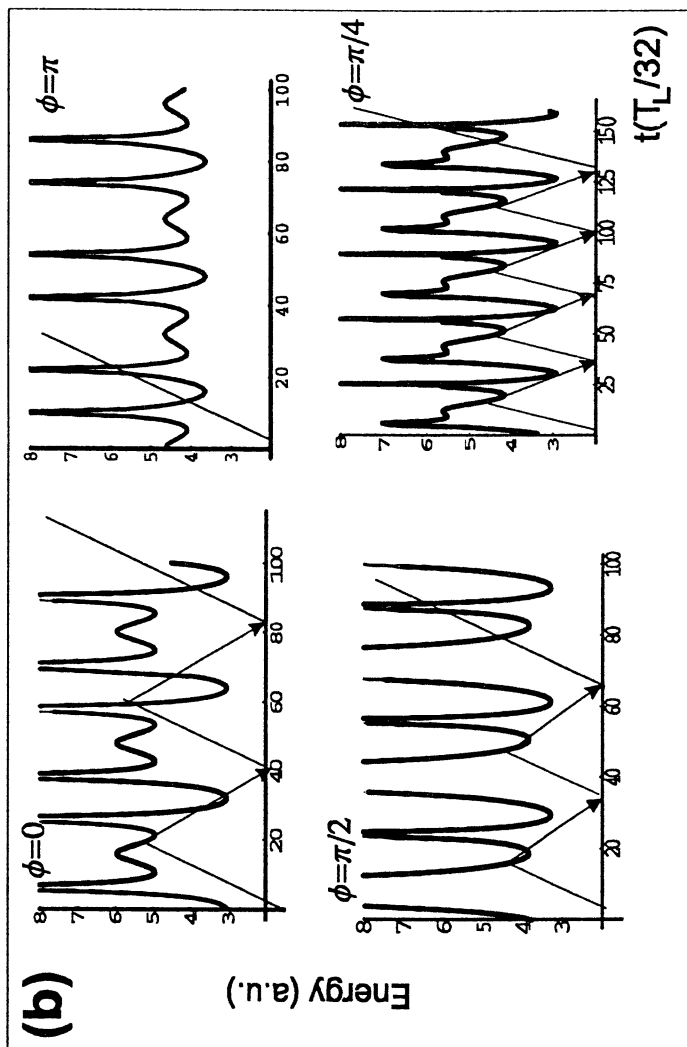$\delta = 0$ *and* $\phi = 0, \pi/4, \pi/2, \pi$.

Figure 2(b): Straight-line trajectory of a ballistic particle, modeling HD^+ in the same field as in Figure 2(a), launched at time $t = 0$ towards the moving barrier the position of which is traced by thick solid lines.

and for a fixed absolute phase $\delta = 0$. In Figure 2(b), we show, as a function of time, for HD^+, (treated in the usual two-channel model with but parallel coupling, induced by the field of panel (a), between the lowest two σ orbitals), the position of the potential energy barrier found on the ground-state adiabatic surface $W_-(R,t)$. Like in Figure 1(c), we also show, in the various panels of Figure 2(b), the trajectory of a ballistic particle representing the wavepacket launched on the $W_-(R,t)$ at $t = 0$.

One dimensional wavepacket calculations have been performed for HD^+ under the two-color field with the relative phase ϕ taking on the values illustrated in Figure 2(a). The same methodology and initial conditions as described in our previous work are employed. The results of these calculations are shown in Figure 3(a), for a field frequency $\omega_L = 1680 \ cm^{-1}$, and peak intensity $I = 5 \times 10^{13} \ W/cm^2$. These are to be compared with the results shown in Figure 1(c) for H_2^+ and HD^+ under a one-color excitation. Here, the control parameter is not the field's absolute phase, but the dephasing between the second harmonic and the fundamental waves. We also give, in Figure 3(b), the results obtained for the same two-color fields as in panel (a), but with an absolute phase $\delta = \pi$. Our results demonstrate clearly that roughly the same selectivity (about 50 % of difference) is achieved between $\phi = 0$ and $\phi = \pi$, in this two-color time-asymmetric excitation of HD^+, as found previously between $\delta = 0$ and $\delta = \pi$ in the one-color excitation of the same molecule. This is true for the two choices of the absolute phase illustrated in Figure 3(a) and (b), although in the fine details of the time-resolved dynamics, significant differences exist between these two cases.

The selectivity of the DDQ effect is up to this point limited to about 50 %. It can certainly be improved if we search to optimize the initial stage of the scheme by a tracking control procedure[6], properly adapted to the specific objective we have in mind (initial drop of $P_{bound}(t)$ for instance), and restricted to the type of field such as the two-color field above. Works in this direction are in progress in our laboratory.

Molecular dynamical restructuring in an IR laser field

Principle

In current views of laser-induced molecular restructuring, the instantaneous electronic dipole interaction potential

$$V_{int}^{EF}(\{\vec{r}_i\}) = -e \sum_i \vec{r}_i \cdot \vec{E}(t) \qquad (4)$$

is thought to cause mixing of field-free MOs, $\{\phi_k\}$ themselves constituted of field-free AOs, $\{\chi_j\}$, i.e. $\phi_k(1) = \sum_j c_{kj}\chi_j(1)$, yielding new, field-induced,
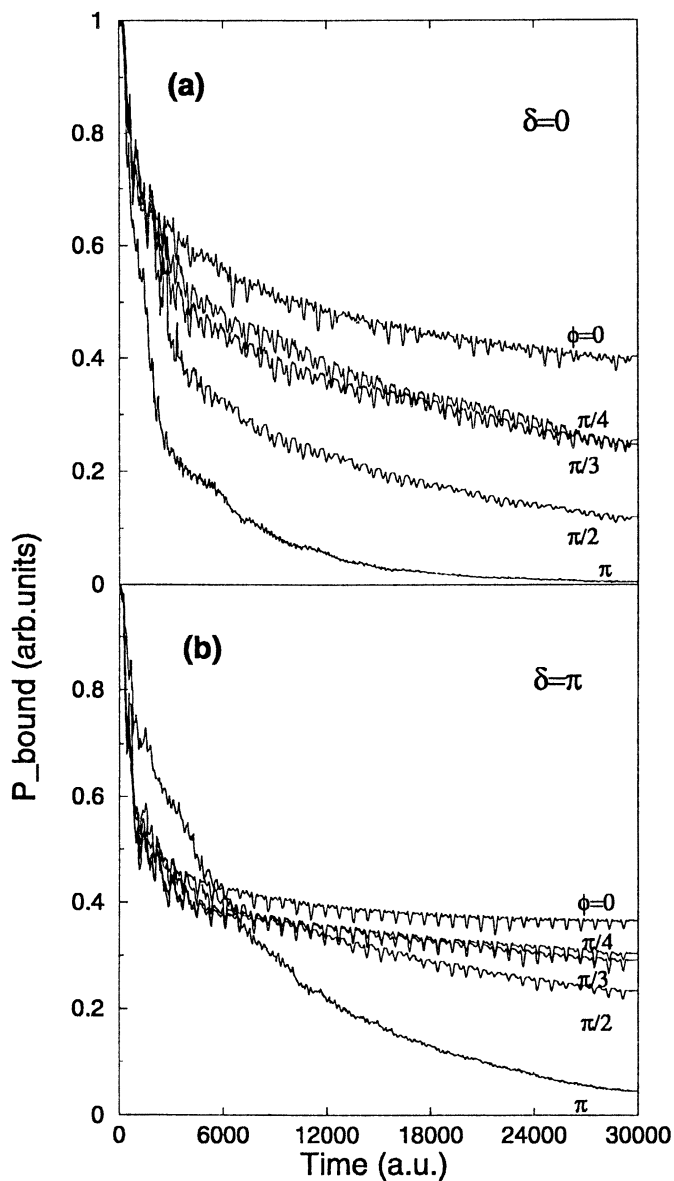
*Figure 3: Time evolution of P_{bound} for HD^+ in an IR,
$I = 5 \times 10^{13}$ W/cm^2 field of the form given in eq.(3) and of varying
relative phase and with (a), $\delta = 0$, (b), $\delta = \pi$.*

time-parameterized MOs, $\{\tilde{\phi}_k\}$, (henceforth, tilded symbols will always denote field-induced orbitals and orbital properties). Alternatively, these field-induced MOs can also be regarded as resulting from the interactions of AOs $\tilde{\chi}_j(1,t)$ that are already shifted and modified by the intense electric field, i.e. satisfying

$$\left[\hat{h}_j^0(c[j]) - e\vec{r}_1 . \vec{E}(t)\right] \tilde{\chi}_j(1,t) = \tilde{\epsilon}_j(t)\tilde{\chi}_j(1,t) \tag{5}$$

where $c[j]$ denotes the atomic center which supports the considered AO, and $\hat{h}_j^0(c[j])$ denotes the one-electron effective hamiltonian defining the field-free atomic orbitals centered on $c[j]$. Among the effects that the linear potential $-e\vec{r}_1.\vec{E}(t)$ has on the AO $\tilde{\chi}_j(1,t)$ and its energy $\tilde{\epsilon}_j(t)$, there always is a geometry-dependent energy shifts $\delta_j = -e\vec{R}_{c[j]}.\vec{E}(t)$ due to the displacement of the nuclear center $c[j]$ from the center of mass, which always is the center with respect to which is defined the electronic dipole moment of the molecule. Often, and in most interesting cases, where $\delta_j \neq 0$, as in the examples of the H_2^+, HD^+ molecules considered above, this shift dominates over the intrinsic atomic Stark shift, so that one expects the changes in the LCAO-MO scheme, as one goes from the field-free to the strong field cases, to be due mainly to this (geometry-dependent) shift. To examine how the shifts δ_j of AOs induce changes in the LCAO-MO structure, through a correlation diagram highlighting the interaction of field-shifted AOs, defines what we call the LCfiAO scheme.

As an example, consider the H_2^+ molecule described in the minimal $\{1s_A, 1s_B\}$ basis and aligned along the polarization direction of the field. In the LCfiAO approach, rather than starting by coupling the field-free $\sigma_{g(u)}$ MOs together, we would consider the interaction between the field shifted AOs $\widetilde{1s}_A(t), \widetilde{1s}_B(t)$[7] of energy (in atomic units) $\tilde{\epsilon}_{A(B)} = -1/2 \pm RE(t)/2$. Diagonalizing the hamiltonian matrix, $\tilde{H}(R,t)$ in this basis, we obtain the same (time-)adiabatic eigenvalues, $(W_\pm(R,t))$, as obtained in eq.(2).

Molecular restructuring of H_2O

We now apply the LCfiAO principle to a H_2O molecule subjected to an IR laser field linearly polarized along the C_2 symmetry axis of the molecule. This amounts to assuming that the molecule has been prealigned by the field through its interaction with the permanent-dipole[8]. Figure 4 shows, for a C_{2V} geometry close to the field-free equilibrium geometry, the typical correlation diagrams depicting the laser-induced MO formation from the field-shifted AOs, (I) in the case $\vec{\mu}.\vec{E} < 0$, corresponding to an antiparallel orientation of the molecule's permanent dipole moment $\vec{\mu}$ with respect to the instantaneous field (right panel), and (II) in the case $\vec{\mu}.\vec{E} > 0$ corre-
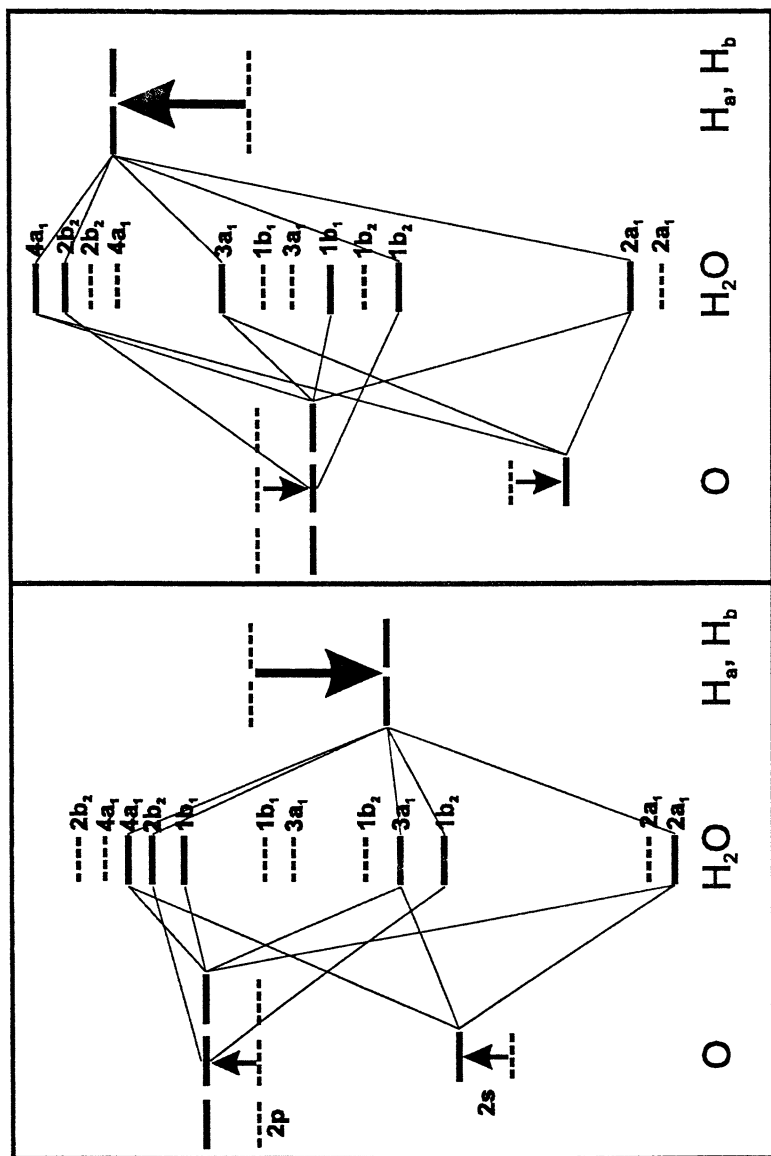
Figure 4: Correlation diagram illustrating the formation, by the LCftAO principle, of molecular orbitals in H_2O in a static electric field with polarization vector oriented anti-parallel to the molecule's permanent dipole moment (left panel), and parallel to that moment (right panel).

sponding to a parallel configuration of $\vec{\mu}$ with respect to the instantaneous electric field (left panel).

Case I: Antiparallel orientation

In the case I, (right panel of Figure 4), the hydrogen $1s$ levels are strongly lowered while the oxygen $2s$ and $2p$ levels are shifted upward, by an amount less than the shift of the H levels, as the oxygen atom lies closer to the center of mass of the molecule. As a consequence of these shifts, all the bonding orbitals, the $2a_1$ and the $1b_2$ MOs, see their hydrogen $1s$ content increases, and are stabilized while their antibonding counterparts, the $4a_1$ and $2b_2$ MOs, should see their LCAO composition more dominated by the oxygen's $2p$ orbitals of appropriate symmetry. The $3a_1$ MO is expected to be lowered and to contain a more appreciable contribution of the hydrogen $1s$ a_1 symmetry-adapted combination. Overall, these changes in the MOs' compositions and in their energies result in (i) a lowering of the total energy, (ii) a net polarization of the electronic charge density from the oxygen atom to the hydrogens, (even one of the 'lone pairs', the one occupying the $3a_1$ MO, is now shifted towards the hydrogens). In the limit of a very intense field, and/or at a large OH internuclear distance R, which makes the geometry-dependent shifts δ_i become larger than the shifts due to the AO interaction in field-free condition, the charge transfer from the oxygen atom to the hydrogens would tend to be more and more complete, leading asymptotically to ionic fragments $O_2^{2+} + 2H^-$, and the total energy decreases linearly with E_0 or R. This asymptotic region is expected to be preceded by a region, found at a lower R (and/or E_0), where the intrinsic AO interactions continue to dominate over the geometric shift effect and give rise to bound MOs and a potential well which is separated from the asymptotic region by a barrier for dissociation. Thus one expects that, for a given value of the HOH bond angle θ, the laser-induced adiabatic potential energy curve would look like the W_- curve of the previous section. Moreover, for this antiparallel orientation of the molecule's permanent dipole, the geometric shift effects (charge polarization and energy lowering) are stronger for smaller bond angles, i.e we expect the potential well to be deeper for smaller values of θ.

All these predictions are well borne out by results of *ab-initio* calculations carried out with the option '*field*' of the GAUSSIAN 94 package[9] which allows for the inclusion of a finite field in the form of an external one-electron potential added to the *ab-initio* Fock operator. In so far as no information on ionization rate is required, these calculations are straightforward, and can be made at any level. Figure 5 shows results of calculations made at the Hartree-Fock Self-consistent-field (HF-SCF) level using a $6 - 31G^{**}$ basis, in the form of two-dimensional potential energy surfaces for a H_2O molecule in a static electric field. The upper panels (indicated
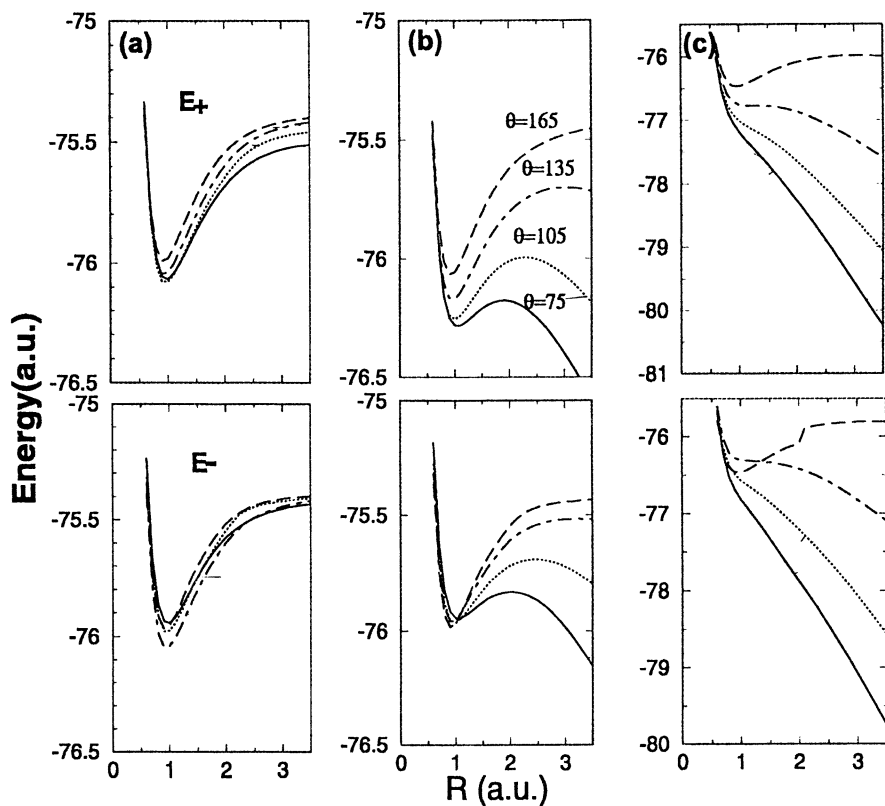
Figure 5: Two-dimensional PESs for a H_2O molecule in a static electric field with polarization vector oriented anti-parallel to the molecule's permanent dipole moment (upper panels), and parallel to that moment (lower panels); (a) $I = 5 \times 10^{13}$ W/cm^2, (b) $I = 4 \times 10^{14}$ W/cm^2, (c) $I = 2 \times 10^{15}$ W/cm^2. The values chosen for θ(deg) are given in (b).

$E+$) refer to the antiparallel configuration of the permanent dipole moment with respect to an instantaneous field of intensity (a) $I = 5 \times 10^{13}\ W/cm^2$, (b) $I = 4 \times 10^{14}\ W/cm^2$, (c) $I = 2 \times 10^{15}\ W/cm^2$. The PES clearly exhibit the features anticipated above.

Case II: Parallel orientation

In the case II of a parallel orientation of the molecule's permanent dipole moment, (left panel in Figure 4), the hydrogen $1s$ levels are strongly shifted upward while the oxygen $2s$ and $2p$ levels are lowered. This time, it is towards the O atom that electronic charge density would flow, resulting in an dissociative asymptotic charge distribution, $O^{2-} + 2H^+$, that is exactly the opposite of what was found for the antiparallel orientation case. What was said above about the overall, generic shape of potential energy curves at a fixed HOH angle remains true, however we would expect deeper potential wells at larger rather than at smaller angles. Also, the strong upward shifts of the hydrogen $1s$ levels would move them somewhat out of 'resonance' with the oxygen AOs, so that we expect the bonding character of all occupied MOs weakened, i.e the energy at a given geometry would tend to increase with respect to the field free situation, (it would certainly be larger than in the antiparallel case), a tendency which is smaller at larger values of θ and smaller R.

The lower panels of Figures 5(a)-(c) show the two-dimensional(2D) PES obtained in our ab-initio calculations for this case. At lower intensities, the predictions spelled out above seem to be verified to some extent: There indeed is a shift of the potential well toward a larger θ, although, in Figure 5(b), the 2D PES appears to exhibit rather an almost flat valley with respect to the varying bond-angle. At the level of the present ab-initio calculations,the potential wells in this configuration are about one eV higher than those obtained in case I above.

Laser-induced asymmetric force field

The results shown above, of the ab-initio calculations of molecular orbitals of H_2O in a IR laser field polarized along the molecular C_2 symmetry axis, and of the correlation diagram describing the LCfiAO-MO scheme for this laser-driven system demonstrate clearly that the first ingredient for the DDQ effect to operate in this case does indeed exists: The 2D PESs found above for the two configurations of the molecular permanent dipole moment with respect to the instantaneous electric field vector, corresponding to two different stages of the field oscillation, or two different times within an optical cycle, exhibit the precise time-asymmetry needed for a control scheme

of the DDQ type to be possible. There are certainly alignment situations for which such a natural time asymmetry would not be possible, but given a polyatomic molecular system, there always exists a configuration (molecular alignment) which offers this opportunity to control the dynamics by a DDQ-like effect. In the case of H_2O, the alignment of the molecular permanent dipole moment along the field polarization is the necessary condition for a time-asymmetric laser-induced force field to exist and to give rise to a DDQ-like effect. Once this alignement is assured by the proper choice of laser intensity range, we can imagine the wavepacket dynamics being steered to favor one or the other dissociative pathway, using a two-color excitation for example.

Acknowledgements

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