MOLECULES IN INTENSE LASER FIELDS

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The US National Science Foundation (NSF) has recently announced in this "Year of Light" that Optics and Photonics is "a key enabling technology that will impact future society in a multitude of areas". Strong field physics of molecules via new intense ultrafast laser technologies is one of the new promising areas of research in this new scientific direction through advances in current laser technology which provide new tools to explore a new regime of light-matter interaction, the nonlinear nonperturbative interaction of atoms and molecules with intense ($I \geq 10^{14}$ W/cm^2) few cycle laser pulses. In the atomic case new nonperturbative optical phenomena have been found such as above threshold ionization (ATI), tunnelling ionization which is the basis of recollision physics [1]. Another important nonlinear process, high order harmonic generation (HHG) is the current main source of attosecond (1 asec $= 10^{-18}$s) pulses necessary to image and control the quantum nature of electrons in matter [2]. This rapid development of ultrashort intense laser pulses allows for shaping and focussing such pulses to higher intensities I (W/cm^2) with corresponding electric fields exceeding the atomic unit (a.u.) $E_0 = 5 \times 10^9$ V/cm at the 1s H atom orbit radii $1a_0 = 0.0529$ nm or equivalently the a.u. of intensity $I_0 = 3.5 \times 10^{16}$ W/cm$^2 = cE_0^2/8\pi$ (Table 1). Such high intensities result in rapid ionization of atoms and molecules, through tunnelling ionization and barrier suppression. The Schwinger limit, $I_s = 10^{29}$ W/cm^2 is the limit of instability of the vacuum itself through tunnelling ionization, creating electron (e^-)-positron (e^+) pairs which in the presence of multi-center molecular systems can occur at $I = 10^{24}$ W/cm^2 [3]. The intensities discussed in this article, $10^{14} \leq I \leq 10^{15}$ W/cm^2 correspond to fields approaching the internal Coulomb potential V_0 or corresponding electric fields E_0 (Table 1) in atom and molecules, thus introducing considerable distortion of atomic and intermolecular potentials [4].

SUMMARY

Molecules exposed to intense laser pulses differ from atoms. One nonlinear response is *Enhanced Ionization* at critical internuclear distances. This leads to Coulomb explosion for imaging molecular structures and nuclear fusion.

TABLE 1
ATOMIC UNITS ($e = \hbar = m_e = 1$, $c = 137$).

potential energy	$V_0 = e^2/a_0 = 1$ Hartree $= 27.2$ eV
electric field	$E_0 = e/a_0^2 = 5.14 \times 10^9$ V/cm
intensity	$I_0 = cE_0^2/8\pi = 3.5 \times 10^{16}$ W/cm^2
distance	$a_0 = 0.0529$ nm $= 0.529$ Å
velocity	$v_0 = 2.19 \times 10^8$ cm/s $= c/137$
time	$t_0 = a_0/v_0 = 24.2 \times 10^{-18}$ s $= 24.2$ asec
	$t_c = \hbar/m_e c^2 = 1.29 \times 10^{-21}$s $= 1.29$ zeptosec

Using a "dressed" photon state representation which includes photon states on equal level with molecular states, one obtains at high intensities laser induced molecular potentials with the appearance of a new phenomenon, "bond-softening" through laser induced avoided crossings of molecular potentials. At the above high intensities one needs to consider further ionization and above threshold dissociation (ATD), the equivalent of ATI in atoms [5].

A fundamental difference appears when comparing molecules to atoms in intense laser fields. The quasi-static picture of atomic tunnelling ionization [1,2] needs to be modified in view of the multi-center nature of electron potentials in molecules due to the presence of large electronic transition moments, originally discussed by Mulliken as charge resonance (CR) transitions [5,6]. Such

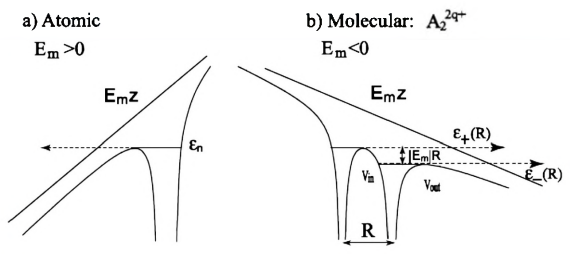

Fig. 1 Above barrier ionization in (a) atoms and (b) molecules via Stark shifted LUMO, $\varepsilon_+(R)$ and HOMO, $\varepsilon_-(R)$. $E_m z$ is the static field energy of an electron at position z in the presence of the field E_m.

large radiative coupling leads to "enhanced ionization" at large critical internuclear distance R_c which can be predicted from quasi-static models of field distorted intermolecular potentials, as illustrated in Fig. 1. The basic physics of such models which differs fundamentally from quasi-static atomic tunnelling ionization is the ultrafast localization of electrons on atoms by adiabatic charge-transfer at electric field maxima across the whole length of the molecule.

QUASI-STATIC MODEL OF DIATOMIC MOLECULES

The first simple analytic formulae for atomic multiphoton ionization beyond usual perturbation (Fermi-Golden rule) theory was obtained by Keldysh [7] who showed that the Keldysh parameter γ allows separation of the perturbative multi-photon regime from a nonperturbative high intensity quasi-static tunnelling regime. This parameter is defined as

$$\gamma = \sqrt{\frac{I_p}{2U_p}}, \tag{1}$$

where I_p is the ionization potential and U_p is the ponderomotive energy, $U_p = I_0/4\omega^2$ (a.u.), the average kinetic energy of a free electron in a linearly polarized field $E(t) = E_0 \cos(\omega t)$. The maximum excursion of such an electron is defined by a ponderomotive radius

$$\alpha_d = E_0/\omega^2; U_p = \alpha_d^2\omega^2/4 = E_0^2/4\omega^2. \tag{2}$$

The Keldysh parameter γ in Eq. (1) is the ratio of two energies: I_p the minimum energy to ionize the electron and $2U_P$, the maximum energy $m_e v^2/2$ acquired by an electron in the laser field [8].

The quasi-static model allows for establishing the critical or minimum electric field E_m when "above threshold" ionization occurs. This is illustrated in Fig. 1(a) for a one-electron atom and Fig. 1(b) for the single valence electron diatomic molecule H_2^+ in the presence of a static electric field E. In the atomic case with an effective nuclear charge $q+$, the total potential along the z axis is $V(z) = -q/|z| - Ez$. The electron field distorts the atomic Coulomb potential thus producing a barrier with a maximum at $z_m = (q/E_m)^{1/2}$. With $V(z_m) = -I_p$, the orbital energy, one obtains the minimum field $E_m = I_p^2/4q$ for above-barrier ionization. Since $I_p = q^2/2n^2$ for hydrogen-like atoms at principal quantum number n, then $E_m = q^3/(2n)^4$ (in a.u.) or intensity $I_m = cE_m^2/8\pi = cq^6/8\pi(2n)^8$. Thus for H($n = 1$), $I_p = 0.5$ a.u. and $I_m = 1.4 \times 10^{14}$ W/cm^2. For the Th^{+89} ion in its $n = 2$ level, $I_m = 2.8 \times 10^{23}$ W/cm^2. Such superintense fields are being currently developed in the European ELI (Extreme Light Infrastructure) project and at ALLS (Advanced Laser Light Source) at INRS-EMT (Varennes, Quebec). The theoretical description of such superintense field electron ionization requires applying the time-dependent Dirac equation to include relativistic effects such as pair production [3].

Figure 1 illustrates the essential difference in the highly nonlinear, nonperturbative response between a single center atomic system (Fig. 1(a)) such as the H atom and a two center molecular system, H_2^+ (Fig. 1(b)). Tunnelling ionization and laser induced recollision occur directly in the atomic case for which a simple analytic semiclassical theory predicts a maximum recollision energy $E_r = I_p + 3.17U_p$ [8]. In the molecular case, the highest molecular orbital HOMO, is downshifted by a Stark effect whereas the lowest unoccupied orbital, LUMO is upshifted by the same Stark effect, equal to $ER/2$ for an electric field E at internuclear distance R. Both classical and quantum descriptions arrive at the same result, the first as the difference in potential energy $\pm ER/2$ between each site or as radiative transition, $ER/2$ between the HOMO and LUMO.

Exact quantum mechanical calculations based on the time-dependent Schrödinger equation (TDSE) are illustrated in Fig. 2(a) for H_2^+ vs R at intensities $I = 10^{14}$ W/cm^2 for linear and circular polarizations at different laser polarization-molecular axis orientations. Figure 2(b) reports a new simulation for laser circular polarization in the molecular (x, z) plane.

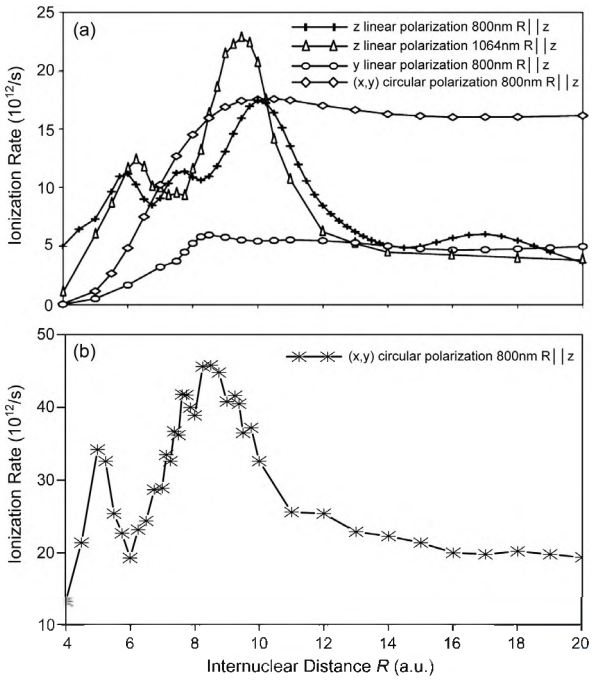

Fig. 2 Ionization rates for H_2^+ vs R. Five cases are taken into account: panel a, (i) z linear polarization at $\lambda = 800$ nm (+) and (ii) at $\lambda = 1064$ nm (Δ); (iii) y linear polarization at $\lambda = 800$ nm ($\circ$); (iv) circular polarization in the (x, y) plane at $\lambda = 800$ nm ($\diamond$); and panel b, (v) circular polarization in the (x, z) plane at $\lambda = 800$ nm ($*$). R is always parallel to the z axis and the pulse intensity is fixed at $I = 10^{14}$ W/cm^2.

In all cases a double peak structure in the ionization rate is obtained with a major peak at $R \approx 10$ a.u. Of note is that for the molecular (x, z) plane circular polarization case, a similar double peak structure is obtained as for linear polarization. It has been shown previously that laser circular polarization fields are equivalent in a frame rotating at the laser frequency to static electric fields with additional Coriolis forces [9]. At low frequencies where tunnelling ionization models allow for accurate predictions [7,8], Coriolis forces are negligible so that static field models become applicable also in circular polarization, thus confirming the generality of static field models for ionization of molecules in intense laser fields.

Enhanced ionization of molecules with intense ultrashort laser pulses was predicted as early as 1995 based on the simple static field model illustrated in Fig. 1 [4]. The double peak structure has now been confirmed by careful experiments twenty years later due to advanced ultrafast laser technology [10], thus providing an important concept and model in the strong field physics of molecules. Dissociation of molecular ions by intense electric and magnetic fields was considered already fifty years ago for applications in particle accelerators [11]. Current laser technology as discussed in the introduction allow for the generation of such intense electric fields in the highly nonlinear, nonperturbative regime. Of interest to this new emerging direction in strong field physics is the applicability and use of a quasi-static model of radiative interaction between laser fields and matter. Molecular media have been ideal systems for applying and exploring strong field quasi-static models in laser induced electron diffraction (LIED) for molecular structure imaging [12], nuclear fusion [13], and pair production in superintense laser fields [3].

A recent new discovery in strong field physics is the unequal transfer of photon momentum to both the ionized electron and the parent ion [14]. In the case of one photon ionization, such an effect was used in astrophysics to explain the presence of certain ions at the surface of stars [15]. In strong fields, multiphoton absorption can result in large momentum transfer unequally to the electron and ion. In molecules this will require considering new nonadiabatic effects between electrons and nuclei mediated by photon absorption in order to make "electronic movies" with strong laser fields [16,17].

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