Alignment-Dependent Ionization of Molecular Hydrogen in Intense Laser Fields

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The alignment dependence of the ionization behavior of H₂ exposed to intense ultrashort laser pulses is investigated on the basis of solutions of the full time-dependent Schrödinger equation within the fixed-nuclei and dipole approximation. The total ionization yields as well as the energy-resolved electron spectra have been calculated for a parallel and a perpendicular orientation of the molecular axis with respect to the polarization axis of linear polarized laser pulses. For most, but not all considered laser peak intensities the parallel aligned molecules are easier to ionize. Furthermore, it is shown that the velocity formulation of the strong-field approximation predicts a simple interference pattern for the ratio of the energy-resolved electron spectra obtained for the two orientations, but this is not confirmed by the full ab initio results.

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Time-resolved imaging of the dynamics of nuclei and electrons on a femtosecond or even sub-femtosecond time scale is a prerequisite for the real-time investigation of the formation and breaking of chemical bonds. Ultrashort laser pulses have recently been demonstrated to pave a possible path to the experimental realization of this long-standing dream. For example, ways have been proposed and experimentally verified that allow monitoring nuclear motion with sub-femtosecond and sub-Ångström resolution in real time [1, 2, 3]. It was also experimentally demonstrated that the high-harmonic radiation or the electrons emitted in an intense laser pulse may in principle reveal information on the electronic structure [4, 5] and thus have the potential for time-resolved imaging of changes of the electronic structure in, e.g., a chemical reaction. To reach this goal it is, however, important to understand the relation between electronic structure and the strong-field response of molecules. This includes the fundamental question whether the rather clear correspondence between the symmetry of the highest-occupied molecular orbital (HOMO) and the strong-field signal as indicated for N₂ and O₂ in [4, 5] is really a universal phenomenon.

Already some time ago it was found that within the molecular strong-field approximation (MO-SFA) — formulated in velocity gauge (VG) and within the framework of a linear combination of atomic orbitals (LCAO) — the molecular response to intense laser fields should reflect the symmetry of the highest occupied molecular orbital (HOMO) [6, 7]. In the case of diatomic molecules, a simple interference picture arises in the MO-SFA-VG that seems to plausibly explain the occurrence or absence of suppressed ionization [6]. The term suppressed ionization describes the effect that a molecule with the same ionization potential as the one of some so-called companion atom is harder to ionize in an intense laser pulse. For example, molecular nitrogen shows a similar ionization behavior as atomic Ar, while the ionization yield of oxygen is much smaller than the one of Xe atoms; despite the almost identical ionization potentials of either N₂ and Ar or O₂ and Xe. Although suppressed ionization is also predicted by tunneling models like molecular Ammosov-Delone-Krainov (MO-ADK) [8] or the length-gauge formulation of the MO-SFA [9], these theories do not provide a simple interference picture for the effect. On the other hand, the energy-resolved electron spectra measured in [10] seemed to further support the concept of symmetry-induced quantum-interference effects as predicted by MO-SFA-VG.

One key step towards time-resolved imaging is the measurement of the molecular strong-field response within a molecule-fixed coordinate system. This is also the basic difference between the electron spectra measured in [5] in comparison to the ones in [10]. While the former are obtained as a function of the alignment between the molecular axis and the laser-field axis, the latter are averaged over all orientations. This explain the increased recent interest even in alignment-dependent total ionization yields of molecules in intense laser pulses [11, 12, 13]. In fact, the results in [11] seem to indicate that, at least for N₂ and O₂, structural information (on the HOMO) may be obtained already from such integral, but angular-resolved ion yields. Besides the problem that the results obtained in [11] for CO₂ seem to be difficult to interpret as a simple mapping of its HOMO, already relatively simple diatomic molecules like O₂ and N₂ possess a HOMO that is not necessarily well described as a linear combination of two atomic orbitals, as is easily seen from the recent debate about the prediction of MO-SFA-VG for the parallel to perpendicular strong-field ionization yield of N₂ (see [14] and references therein). Therefore, molecular hydrogen with a comparatively simple orbital structure and the lack of core orbitals that may disturb the strong-field response appears to be a perfect candidate to investigate whether the interference effects predicted by MO-SFA-VG occur. Furthermore, H₂ has at
least for fixed nuclei now become accessible to in principle exact theoretical calculations, even for a non-parallel orientation of the molecular axis with respect to the field that requires a full 6-dimensional treatment \[15\]. Its extension to laser fields with a wavelength of 800 nm and the extraction of energy-resolved electron spectra is reported in this work.

In fact, the purpose of this Letter is threefold. First, the alignment dependence of the total ionization yield of H\(_2\) in intense laser pulses with a wavelength of about 800 nm (Ti:sapphire) is investigated by means of a full solution of the time-dependent Schrödinger equation (TDSE) describing both correlated electrons in full dimensionality within the fixed-nuclei and the non-relativistic dipole approximations. It is shown that the ratio of ionization yields for parallel and perpendicular alignment is a non-monotonic function as a function of laser peak intensity, even if focal-volume averaging is performed, and is in reasonable agreement to a recent experiment \[12\]. Second, it is demonstrated theoretically that MO-SF A-VG predicts a clear interference pattern in the ratio of energy-resolved electron spectra for a parallel and a perpendicular alignment of a molecule like H\(_2\). Finally, the corresponding energy-resolved electron spectra are extracted from the TDSE calculation and it is demonstrated that the simple interference pattern predicted by MO-SF A-VG is not confirmed.

Figure 1 shows the ionization yields for a parallel and a perpendicular orientation of H\(_2\) exposed to a 800 nm laser pulse as a function of laser peak intensity (for a fixed internuclear separation \(R = 1.4 \, a_0\)). As in all calculations shown in this work 10-cycle \(\cos^2\)-shaped laser pulses (\(\sim 10\) fs FWHM) are used. The numerical approach for solving the TDSE of H\(_2\) has been described recently \[15\]. It is based on an expansion of the time-dependent wavefunction in terms of box-discretized field-free eigenstates obtained from a configuration-interaction calculation based on \(\text{H}_2^+\) eigenstates calculated in a B-spline basis. According to Fig. 1 the ionization yields show evident structures from resonantly-enhanced multiphoton ionization (REMPI) and channel closings, despite the rather high intensity and long wavelength. Since these structures depend on the orientation (the selection rules lead to different REMPI intermediate states and the different polarizabilities to different shifts of the multiphoton thresholds), the results for parallel and perpendicular orientation vary differently as a function of intensity. This is especially evident, if the ratio between parallel and perpendicular alignment is considered (Fig. 2). This ratio shows a highly oscillating structure. Noteworthy, in a certain intensity range the perpendicular alignment leads to a larger ionization yield that the parallel one. A small variation of the wavelength within 780 and 810 nm confirms that even the fine details of the structures are reproducible and not some numerical artifact. Although focal-volume averaging damps the sharp structures, the ratio remains non-monotonous and in some peak intensity regime the perpendicular orientation is easier to ionize than the parallel one.

Very recently, the ratio of the ionization yields for parallel and perpendicular alignment was measured for 800 nm laser pulses in \[12\]. The results are also shown in Fig. 2. Note that the intensities have been adopted as in \[12\], although the experiment was performed with circular polarized light. This is in agreement to the analysis in \[12\] that compared to a model for linear polarization.
using unscaled intensities. Supported also by the present finding, the authors of [12] argued that due to experimental reasons the found anisotropy may be underestimated. Dividing the TDSE results by a factor 1.18 gives in fact a very satisfactory agreement between theory and experiment. Although not really statistically relevant in view of the error bars, one may note that also the experimental data indicate a small local maximum whose exact position depends according to the present TDSE results on the exact wavelength. In [12] a simplified MO-SFA-LG model is also proposed that considers basically the different polarizabilities of H₂ for parallel and perpendicular orientation. The model is in the intensity regime shown in [12] in good overall quantitative agreement with the present TDSE result, but does not show the small minimum. More importantly, it appears unlikely that the model could explain the sharp decrease and even inversion of the ratio for slightly smaller intensities.

In the case of a homonuclear diatomic molecule with internuclear separation R and bonding HOMO Φ built from s-type atomic orbitals φ is given within the LCAO as

$$\Phi(r, R) = a \{ \phi(r, -R/2) + \phi(r, R/2) \}$$  \hspace{1cm} (1)

where r is the electronic coordinate and a the normalization constant. According to MO-SFA-VG [6] (also called first-order IMST) this leads to the N-photon ionization rates (integrated over the directions of the emitted electron)

$$\Gamma_N = N_e \int d\mathbf{k}_N \frac{dW^{(N)}}{d\mathbf{k}_N}$$  \hspace{1cm} (2)

in a linearly polarized laser field, if the HOMO is occupied by N_e electrons. The in Eq. (2) occurring differential ionization rates are given by

$$\frac{dW^{(N)}}{d\mathbf{k}_N} = 2\pi C^2 k_N (U_p - N\omega)^2 J_N^2 \left( \alpha_0 \cdot \mathbf{k}_N, \frac{U_p}{2\omega} \right) \times 2a(|\mathbf{k}_N|) |\phi|^2 \cos^2(\mathbf{k}_N \cdot \mathbf{R}/2).$$  \hspace{1cm} (3)

Here, $k_N^2/2 = N\omega - (U_p + E_{\text{ion}})$ is the kinetic energy of an electron after absorption of N photons, $U_p = F^2/(4\omega^2)$ is the ponderomotive energy of an electron in a laser field of frequency $\omega$ and peak field strength $F$, $E_{\text{ion}} = k^2/2$ is the ionization energy of the molecule, and $C^2 = (\kappa^2/F)^{2/\kappa}$ is a Coulomb correction factor. Finally, $(\mathbf{k}|\phi)$ is the Fourier transform of the atomic orbital $\phi(r)$ and $J_n(a, b)$ is a generalized Bessel function of two arguments as defined in [14]. The polarization axis $\varepsilon$ enters the ionization rate only through one of the arguments of the Bessel function, $\alpha_0 = (F/\omega)^2 \varepsilon$.

The sum of the N-photon ionization rates for all energetically allowed values of N yield the energy-resolved electron spectra also known as above-threshold ionization (ATI) spectra. Since the Fourier transform of spherically symmetric (s-type) orbitals is also spherically symmetric, it depends only on $k$. Therefore, the ratio of the N-photon ionization rates for parallel and perpendicular orientations of the field polarization vector with respect to the internuclear axis can be written as

$$X_N = \frac{\alpha_{||}}{\alpha_{\perp}} = \frac{\int d\mathbf{R} J_0^2 (gN, b, \mathbf{R}) \cos^2 \left( \frac{dN\mathbf{R}}{2} \right)}{\int d\mathbf{R} J_0^2 (gN, b, \mathbf{R}) \cos^2 \left( \frac{dN\mathbf{R}}{2} \right)}$$  \hspace{1cm} (4)

where $gN = \alpha_0 k_N$, $b = U_p/(2\omega)$, $dN = Rk_N/2$, and all factors depending only on the absolute value of $k_N$ were taken out of the integral and cancel each other when the ratio is considered.

Fixing the coordinate system in such a way that its z axis agrees with the polarization vector $\varepsilon$, one has $\mathbf{R}_{||} = (0, 0, 1)$, $\mathbf{R}_{\perp} = (1, 0, 0)$, and $\mathbf{k} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. Then the ratio (4) can be rewritten as

$$X_N = \frac{\int_0^{\pi} \sin \theta J_0^2 (gN \cos \theta, b) \cos^2 (dN \cos \theta)}{\int_0^{\pi} \sin \theta J_0^2 (gN \cos \theta, b) [1 + J_0(2dN \sin \theta)]/2}$$  \hspace{1cm} (5)

where the identity

$$\int_0^{2\pi} d\phi \cos^2(\delta \cos \phi) = \pi [1 + J_0(2\delta)]$$  \hspace{1cm} (6)

for zero-order Bessel function of the first kind was used. For very strong fields the function $J_0^2 (gN \cos \theta, b)$ peaks usually sharply around $\cos \theta = \pm 1$ (i.e. in the case of ionization from a spherically symmetric atom the vast majority of electrons are ejected parallel to the laser polarization axis). On the other hand, the functions $\cos^2(dN \cos \theta)$ and $J_0(2dN \sin \theta)$ vary rather slowly in these regions. They may thus be approximated by their values at $\cos \theta \approx \pm 1$:

$$\cos^2(dN \cos \theta) \approx \cos^2(dN), \quad J_0(2dN \sin \theta) \approx 1.$$  \hspace{1cm} (7)

Substitution of Eq. (7) into Eq. (5) results finally in a very simple expression for $X_N$,

$$X_N \approx \cos^2(dN) = \cos^2(Rk_N/2).$$  \hspace{1cm} (8)

Note, that for very small $dN$ (which means small $R$ or small $k_N$) both functions in Eq. (7) are equal to 1, so the ratio $X_N$ is also 1.

According to Eq. (8) MO-SFA-VG predicts a pronounced minimum to occur at the electron energy $E \approx \pi^2/(2R^2)$, if the ratio between the the energy-resolved electron spectra obtained for a parallel and a perpendicular orientation is considered. Its origin is a pure interference phenomenon that is due to the destructive interference caused by the phase shift between two electronic wave packets emerging from the two nuclei and moving along the polarization axis.
Despite all these attempts to find perfect conditions for finding the interference minimum predicted by MO-SFA-VG, the ratio of the electron spectra for the two orientations does not show the behavior predicted by MO-SFA-VG in Eq. (5) (that agrees well to the approximate expression (8)) as can be seen from Fig. 4. It is interesting that the TDSE results indicate in fact a rather universal overall behavior of the ratio independent of the laser intensity. However, the ratio first increases with increasing electron energy and remains on average above unity. As is clear from Fig. 3, the total ionization yield stems dominantly from the very low-energy electrons. In this regime the ratio between the electron spectra for parallel and perpendicular is, however, rather intensity dependent. This explains the already discussed intensity dependence of the total yield found already at the equilibrium distance.

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