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Alignment-dependent ionization of molecular hydrogen in intense laser fields

Yulian V. Vanne and Alejandro Saenz
AG Moderne Optik, Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

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The alignment dependence of the ionization behavior of H_2 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 a 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, methods have been proposed and experimentally verified that allow monitoring nuclear motion with sub-femtosecond and sub-angstrom resolution in real time [1–3]. It was also experimentally demonstrated that the high-order 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, for example, 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 N_2 and O_2 in Refs. [4,5] is really a universal phenomenon.

Some time ago, it was already found that within the molecular strong-field approximation (MO-SFA)—formulated in a 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 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 for Xe atoms; despite the almost identical ionization potentials of either N_2 and Ar or O_2 and Xe. Although suppressed ionization is also predicted by tunneling models such as molecular Ammosov-Delone-Krainov [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 Ref. [10] seemed to further support the concept of symmetry-induced quantum-interference effects as predicted by MO-SFA-VG.

One key step toward 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 Ref. [5] in comparison to the ones in Ref. [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 explains the increased recent interest in alignment-dependent total ionization yields of molecules in intense laser pulses [11–13]. In fact, the results in Ref. [11] seem to indicate that, at least for N_2 and O_2, structural information (on the HOMO) may already be obtained from such integral, but alignment-resolved ion yields. In addition to the problem that the results obtained in Ref. [11] for CO_2 seem to be difficult to interpret as a simple mapping of its HOMO, relatively simple diatomic molecules such as O_2 and N_2 already 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 the perpendicular strong-field ionization yield of N_2 (see Ref. [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, H_2 has, at least for fixed nuclei, now become accessible to, in principle, exact theoretical calculations, even for a nonparallel orientation of the molecular axis with respect to the field that requires a full six-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 Rapid Communication.

In fact, the purpose of this Rapid Communication 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), which describes both correlated electrons in full dimensionality within the fixed nuclei and the nonrelativistic dipole approximations. It is shown that the ratio of ionization yields for parallel and perpendicular alignments

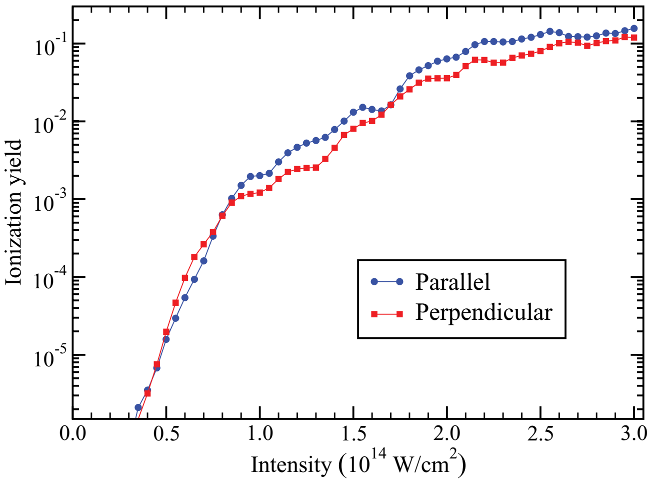

FIG. 1. (Color online) Ionization yields of H_2 (internuclear separation $R = 1.4a_0$) for a ten-cycle $\cos^2$-shaped 800-nm laser pulse and a parallel (blue circles) or perpendicular (red squares) alignment with respect to the laser polarization vector.

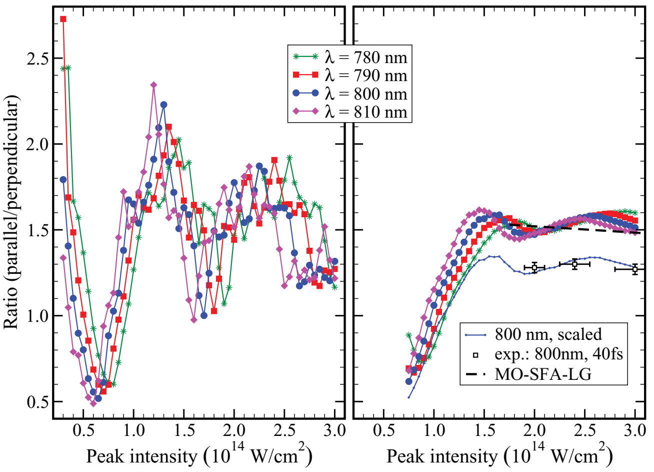

FIG. 2. (Color online) Ratio of parallel to perpendicular ionization yields of H_2 ($R = 1.4a_0$) as a function of laser peak intensity for different wavelengths and ten-cycle $\cos^2$-shaped laser pulses: without (left panel) and with (right panel) focal-volume averaging. For a better comparison to the experimental data from Ref. [12], the 800-nm result is also shown scaled down by a factor 1.18. Furthermore, the (simplified) MO-SFA-LG data in Ref. [12] are depicted.

is a nonmonotonic function as a function of laser peak intensity, even if focal-volume averaging is performed, and is in reasonable agreement with a recent experiment [12]. Second, it is demonstrated theoretically that MO-SFA-VG predicts a clear interference pattern in the ratio of energy-resolved electron spectra for a parallel and a perpendicular alignment of a molecule such as 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-SFA-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 $R = 1.4a_0$). As in all calculations shown in this Rapid Communication, ten-cycle $\cos^2$-shaped laser pulses ($\sim$10-fs full width at half-maximum) 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 wave function in terms of box-discretized field-free eigenstates obtained from a configuration-interaction calculation based on 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 lead 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 alignments 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 than 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 are not some numerical artifact. Although focal-volume averaging damps the sharp structures, the ratio remains nonmonotonous; 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 alignments was measured for 800-nm laser pulses in Ref. [12]. The results are also shown in Fig. 2. Note, that the intensities have been adopted as in Ref. [12], although the experiment was performed with circular polarized light. This is in agreement with the analysis in Ref. [12] in which a comparison was made to a model for linear polarization using unscaled intensities. Also supported by the present finding, the authors of Ref. [12] argued that, due to experimental reasons, the found anisotropy may be underestimated. By 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 also note that the experimental data indicate a small local maximum whose exact position depends, according to the present TDSE results, on the exact wavelength. In Ref. [12], a simplified model based on the molecular strong-field approximation in length gauge (MO-SFA-LG) is also proposed that basically considers the different polarizabilities of H_2 for parallel and perpendicular orientations. In the intensity regime shown in Ref. [12] the model is 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 the inversion of the ratio for slightly smaller intensities.

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

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

where $\mathbf{r}$ is the electronic coordinate and a is the normalization constant. According to MO-SFA-VG [6] (also called first-order intense-field many-body S-matrix theory) this leads to the N-photon ionization rates (integrated over the directions of the emitted electron),

$$\Gamma_N = N_e \int d\,\hat{\mathbf{k}}_N \, \frac{dW^{(N)}}{d\hat{\mathbf{k}}_N}, \qquad (2)$$

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

$$\frac{dW^{(N)}}{d\hat{\mathbf{k}}_N} = 2\pi C^2 k_N (U_p - N\omega)^2 J_N^2\left(\boldsymbol{\alpha}_0 \cdot \mathbf{k}_N, \frac{U_p}{2\omega}\right) \times |2a\langle \mathbf{k}_N|\phi\rangle|^2 \cos^2(\mathbf{k}_N \cdot \mathbf{R}/2). \qquad (3)$$

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 ω and peak field strength F, $E_{\text{ion}} = \kappa^2/2$ is the ionization energy of the molecule, and $C^2 = (\kappa^3/F)^{2/\kappa}$ is a Coulomb correction factor. Finally, $\langle \mathbf{k}|\phi\rangle$ 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 Ref. [16]. The polarization axis ε enters the ionization rate only through one of the arguments of the Bessel function $\boldsymbol{\alpha}_0 = (F/\omega^2)\boldsymbol{\varepsilon}$.

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 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

$$X_N = \frac{\Gamma_N^{\parallel}}{\Gamma_N^{\perp}} = \frac{\int d\hat{\mathbf{k}}\, J_N^2(g_N \boldsymbol{\varepsilon} \cdot \hat{\mathbf{k}}, b)\, \cos^2(d_N \hat{\mathbf{k}} \cdot \hat{\mathbf{R}}^{\parallel})}{\int d\hat{\mathbf{k}}\, J_N^2(g_N \boldsymbol{\varepsilon} \cdot \hat{\mathbf{k}}, b)\, \cos^2(d_N \hat{\mathbf{k}} \cdot \hat{\mathbf{R}}^{\perp})}, \qquad (4)$$

where $g_N = \alpha_0 k_N, b = U_p/(2\omega), d_N = Rk_N/2$, and all factors that depend only on the absolute value of $\mathbf{k}_N$ were taken out of the integral and cancel each other when the ratio is considered.

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

$$X_N = \frac{\int_0^{\pi} d\theta \sin\theta\, J_N^2(g_N \cos\theta, b) \cos^2(d_N \cos\theta)}{\int_0^{\pi} d\theta \sin\theta\, J_N^2(g_N \cos\theta, b)[1 + J_0(2d_N \sin\theta)]/2}, \qquad (5)$$

where the identity,

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

for the zero-order Bessel function of the first kind was used.

For very strong fields, the function $J_N^2(g_N\cos\theta, b)$ 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 $\cos^2(d_N\cos\theta)$ and $J_0(2d_N\sin\theta)$ vary rather slowly in these regions. They may, thus, be approximated by their values at $\cos\theta \approx \pm 1$:

$$\cos^2(d_N\cos\theta) \approx \cos^2(d_N), \quad J_0(2d_N\sin\theta) \approx 1. \qquad (7)$$

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

$$X_N \approx \cos^2(d_N) = \cos^2(Rk_N/2). \qquad (8)$$

Note that, for very small d_N (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. Also, the ratio of parallel to perpendicular total ionization yields obtained with Eq. (8) is always lower than 1, in contrast to experiment and TDSE (see Fig. 2).

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, which emerge from the two nuclei and move along the polarization axis.

In order to investigate the occurrence of this interference phenomenon predicted by MO-SFA-VG, the energy-resolved electron spectra of H_2 were also extracted from the TDSE calculations. In order to amplify the effect, the larger internuclear separation $R = 3.0a_0$ is considered in Fig. 3. This should be an ideal case, since at these distances, the HOMO of H_2 is extremely well described by two hydrogenic $1s$ orbitals. There are, in fact, two more reasons for choosing a larger R value. If the predicted minimum lies at too high energies, rescattering that is not incorporated in the first-order SFA theory could dominate and could cover the interference phenomenon. Furthermore, the energy-resolved spectra obtained from the TDSE calculation converge more easily for lower energies, due to their fast exponential decay. 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 with the approximate expression Eq. (8)] as can be seen from

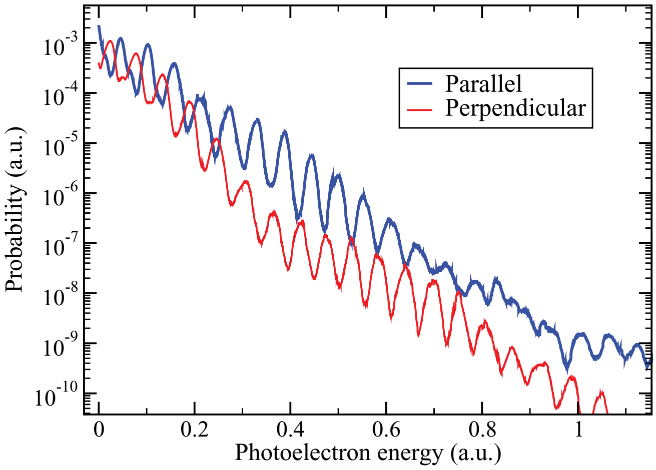

FIG. 3. (Color online) Energy-resolved electron spectra for parallel (blue thick line) and perpendicular (red thin line) orientations of H_2 ($R = 3.0a_0$) for a ten-cycle $\cos^2$-shaped 800-nm laser pulse with a peak intensity of 2×10^{13} W/cm^2.

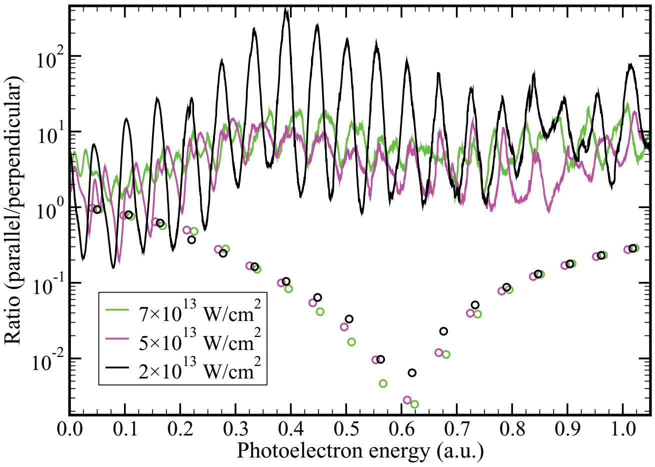

FIG. 4. (Color online) Ratio of parallel to perpendicular energy-resolved electron spectra of H_2 ($R = 3.0a_0$) for a ten-cycle $\cos^2$-shaped 800-nm laser pulse and three different peak intensities. The ratios predicted by MO-SFA-VG in Eq. (5) are also shown using circles.

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 already found at the equilibrium distance.

To summarize, we have calculated total ionization yields and energy-resolved electron spectra for parallel and perpendicular orientations of H_2 molecules in intense 800-nm laser fields. With these results, it was possible to demonstrate a failure of the interference picture predicted by the VG strong-field approximation.

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