Probing H₂ quantum autoionization dynamics with xuv atto and femtosecond laser pulses

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ABSTRACT

We present a theoretical study of dissociative ionization of H_2 and D_2 produced by xuv atto and femtosecond laser pulses. We pay special attention to the analysis of the autoionization dynamics and investigate the effect of the pulse characteristics (spectrum, duration and chirp) on the proton kinetic energy spectrum and the fully differential electron angular distributions. We show that very short pulses, e.g. of 400 as, lead to angular distributions that are nearly independent of the pulse spectral shape and chirp. However, these angular distributions are practically symmetric, which provides little information on the autoionization dynamics. In contrast, for pulses of a few fs, the angular distributions depend significantly on the spectral shape. In particular, when the bandwidth is narrow and the pulse is not chirped, strong asymmetries in the angular distributions are observed. These asymmetries vary with pulse duration, which is relevant to investigate the autoionization decay dynamics of these states.

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1. Introduction

Ultrashort laser pulses produced in high-order harmonic generation (HHG) from atoms and molecules have become a standard tool to investigate ultrafast phenomena. Typical wavelengths and durations of these pulses vary from the vacuum ultraviolet (vuv) to the soft X-ray region, and from the attosecond (as) to the femtosecond time scales. Therefore, they are ideal to induce electronic excitations, including ionization, and to analyze the electron and nuclear dynamics at the atomic time scale. The progressive increase in intensities (from 10^9 up to 10^{14} W/cm²) makes also these pulses ideal to investigate non-linear phenomena [1–3].

The measurement of time-resolved spectra at the atomic/molecular time scales can be used to understand fundamental problems in atomic and molecular physics. For example, recent experiments on rare gas atoms using attosecond xuv pulses have been able to visualize in time the exponential autoionization (Auger) decay of core excited states, which only takes a few femtoseconds [4]. Similarly, attosecond pulses should also be appropriate to investigate the decay of autoionizing states in molecules. This is even more interesting than in atoms because molecular vibrations and dissociation typically occur in the fs time scale and, therefore, can significantly affect the autoionization process [5].

The theoretical description of the dynamics of simple molecules subject to ultrashort laser pulses is still a challenge due to the computational difficulty in accounting for all electronic and vibrational (including dissociative) degrees of freedom. Thus, apart from low dimensionality models (Ref. [6]), most theoretical efforts have concentrated on the simplest molecular ion H_2^+ (Refs. [7,8] and references therein). For H_2, the prototype used in many experiments, theoretical investigations are much scarcer due to the additional difficulty to properly account for electron correlation and the multichannel scattering problem. Autoionization is the result of electron correlation and, consequently, theoretical modeling must thus account for it. Furthermore, since H_2 doubly excited states are dissociative and they autoionize slowly, the nuclei have enough time to move outside the Franck–Condon (FC) region before the electron is effectively ejected (see Fig. 1). Therefore, the theory must also account for the nuclear motion. And last but not least, since direct ionization and autoionization interfere, a fully quantum mechanical treatment of both the electronic and nuclear motions is required.

A time dependent theoretical method that fulfills the above requirements, i.e., that provides a quantum description of electrons and nuclei with inclusion of electron correlation in full dimensionality, has been recently proposed [9,10] and subsequently adapted to treat H_2 autoionization [11,12]. Evidence of autoionization can be found by looking at the fully differential electron angular distributions (FDEAD) for specific orientations of the molecule with respect to the polarization field. This is feasible by performing kinematically complete experiments in which the momentum of

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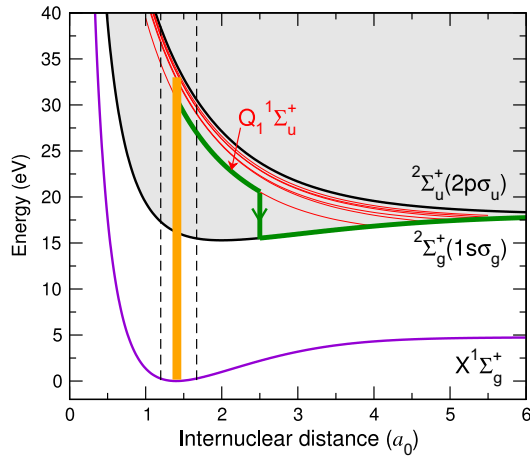
Fig. 1. Potential energy curves of H_2 and H_2^+. Q_1 denotes the lowest $^1\Sigma_u^+$ doubly excited state above the $1s\sigma_g$ threshold. The thick vertical line illustrates absorption of a 33 eV photon. A semiclassical path describing autoionization from the Q_1 state is also shown.

all ejected electrons and atomic ions is determined in coincidence [5,13,14]. The work of Refs. [5,12,15] has shown that the FDEAD can be asymmetric when the H_2 doubly excited states are efficiently populated. This is because ionization channels in which the residual H_2^+ ion is left in states of different inversion symmetry, $1s\sigma_g$ and $2p\sigma_u$, can interfere efficiently due to the delayed ionization from the H_2 doubly excited states. Since the degree of asymmetry depends on this delay, measuring the asymmetry of the photoelectron angular distribution as a function of pulse duration can be used to estimate the corresponding autoionization lifetimes [12].

The latter conclusions were obtained by using pulses with a perfect cosine square shape and null phase. This is an idealistic situation, because, in real experiments, both the pulse characteristics are complicated or even unknown. Also, in many experiments, ultrashort pulses can be chirped, i.e., the frequency varies with time. Thus, in view of ongoing experimental work aimed at investigating H_2 autoionization with ultrashort pulses [16], it is highly desirable to study the effects of the pulse spectral shape, phase and chirp in the measured kinetic energy release (KER) spectra and the FDEAD for different pulse durations. This is the problem we address in this paper. For that, we consider a photon energy of 33 eV and molecules oriented parallel to the polarization direction. Under these conditions, only the lowest Q_1 doubly excited states of $^1\Sigma_u^+$ symmetry are significantly populated (see Fig. 1). We also investigate the differences between H_2 and D_2, because D_2 is preferred in most experiments but, since dissociation takes longer in D_2 than in H_2, the experimental observations could be significantly different in both systems.

Atomic units are used throughout unless otherwise stated.

2. Theory

We have computed the solution of the time dependent Schrödinger equation

$$\left(\mathscr{H}^0(\mathbf{r},R) + V(t) - i\frac{\partial}{\partial t}\right)\Phi(\mathbf{r},R,t) = 0,\qquad(1)$$

where $\mathbf{r}$ represents the electronic coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, R is the internuclear distance, $\mathscr{H}^0$ is the H_2 field-free non-relativistic Hamiltonian

$$\mathscr{H}^0(\mathbf{r},R) = -\nabla_R^2/2\mu + \mathscr{H}_{el}(\mathbf{r},R),\qquad(2)$$

$\mathscr{H}_{el}$ is the electronic Hamiltonian, and $V(t)$ is the laser–H_2 interaction potential in the dipole approximation and velocity gauge

$$V(t) = \mathbf{p} \cdot \mathbf{A}(t).\qquad(3)$$

We used several forms of the vector potential $\mathbf{A}(t)$. For calculations involving a pulse with cosine square shape, we have used

$$\mathbf{A}(t) = \begin{cases} \hat{\mathbf{e}}_\mu \cos^2(\pi t/T) \sum_i A_i \cos[\omega_i(t)(t+T/2)], & -T/2 \leqslant t \leqslant T/2, \\ 0, & \text{elsewhere} \end{cases}$$
$$(4)$$

with T the pulse duration, ω_i the radiation frequency, A_i the vector potential peak intensity defined by

$$A_i = \frac{a_i}{\omega_i}E = \frac{a_i}{\omega_i}\sqrt{\frac{I}{I_{au}}}\qquad(5)$$

in which E is the electric field amplitude, $I_{au} = 3.5095 \times 10^{16}$ W/cm^2 is the atomic unit of intensity, I is the laser field peak intensity, a_i is a dimensionless quantity and $\hat{\mathbf{e}}_\mu$ the polarization vector of the light. The inclusion of a summation in the right-hand side of the above equation allows us to define different pulses representing the following physical situations:

I. One-color radiation: only one term in the summation is used, $a_i = \delta_{i1}$, and ω is independent of time. In this case, ω represents the central photon energy in the spectrum that results from the Fourier transform of $A(t)$. The corresponding full width at half maximum (FWHM) is given by $\Delta\omega = 4\pi/T$.

II. Multicolor radiation: the summation is expanded in several frequencies ω_i independent of time but weighted by the a_i coefficients. The latter satisfy $\sum_i a_i^2 = 1$.

III. Chirped radiation: only one term in the summation is used, $a_i = \delta_{i1}$, and ω is time dependent and its temporal evolution is given by

$$\omega(t) = \omega_0 + (\omega_1 - \omega_0)\sin\left[\frac{\pi}{2T}\left(t + \frac{T}{2}\right)\right].\qquad(6)$$

This formula represents a smooth variation of ω from ω_0 at $t = -T/2$ (the beginning of the pulse) up to ω_1 at $t = +T/2$ (the end of the pulse). This can be used for one or more frequencies.

We have also used more realistic chirped pulses with a much less smooth shape. In particular, we have used attosecond pulses as those produced in recent experimental work [17], in which the shape is the result of specific experimental conditions or is reconstructed from the experimental power spectra, as in [17].

The time dependent wave function $\Phi(\mathbf{r},R,t)$ is expanded in a basis of fully correlated adiabatic Born–Oppenheimer vibronic stationary states of energy W_k, which include the bound states, the doubly excited states and the non-resonant continuum states of H_2:

$$\Phi(\mathbf{r},R,t) = \sum_b \sum_{\nu_b}^f C_{bv_b}(t)\phi_b(\mathbf{r},R)\chi_{v_b}(R)e^{-iW_{v_b}t}$$
$$+ \sum_r \sum_{\nu_r}^f C_{rv_r}(t)\phi_r(\mathbf{r},R)\chi_{v_r}(R)e^{-iW_{v_r}t}$$
$$+ \sum_{\alpha\ell} \int d\varepsilon \sum_{\nu_\alpha}^f C_{\alpha\nu_\varepsilon}^{\varepsilon\ell}(t)\psi_{\alpha\ell\varepsilon}(\mathbf{r},R)\chi_{v_\alpha}(R)e^{-iW_{v_\alpha}t},\qquad(7)$$

where ϕ_b, ϕ_r and $\psi_{\alpha\ell\varepsilon}$ represent the bound, doubly excited and continuum electronic states of H_2, respectively. These electronic states result from the solution of the following eigenvalue equations: