Molecular ionization and dissociation using synchrotron radiation and ultrashort laser pulses

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Abstract. An overview of recent theoretical progress to accurately describe non dissociative and dissociative ionization of molecules exposed to synchrotron radiation and ultrashort uv/xuv laser pulses is presented. The success of recent theoretical approaches rely on their ability to account for both the electronic and nuclear degrees of freedom. This is essential to describe the delicate interplay between the electronic motion and the molecule’s vibration, especially in those cases where ionization occurs in a time scale comparable to that of the vibrational motion. Some of the most successful applications and the new physics that has emerged by comparing with recent kinematically complete experiments on H₂ and D₂ will be discussed.

1. Introduction
Molecular ionization is one of the most elementary processes that occurs in the upper atmosphere [1] and in interstellar molecular clouds [2]. Since in molecules the absorbed energy is shared between electronic and nuclear degrees of freedom, the remaining molecular ion can be left in an excited vibrational or dissociative state. This is at variance with atomic ionization where the energy is entirely absorbed by the electrons. In early pictures of molecular ionization, the nuclear motion was either ignored or described in terms of the Franck-Condon (FC) approximation, in which electronic processes occurring at the equilibrium position of the nuclei are weighted by the squared overlap between the initial and final vibrational states. With the advent of kinematically complete experiments [3, 4], in which the momenta of all charged particles is determined, new phenomena with an intrinsic molecular origin have been discovered (see, e.g., [5–11]). Also the above pictures have been revealed to be incomplete. In this manuscript, the important role of nuclear dynamics in molecular ionization produced by synchrotron radiation and ultrashort pulses will be demonstrated by means of recent ab initio theoretical calculations that account for all electronic and vibrational degrees of freedom.

In particular, recent results for electron angular distributions from fixed-in-space molecules will be analyzed and compared with kinematically complete photoionization experiments using synchrotron radiation. These include double and single photoionization of H₂ (D₂). The range of excess photon energies considered goes from a few to several hundreds of eV. Also, multiphoton ionization of molecules by vuv ultrashort pulses will be discussed. In particular, the new physics that can be expected by varying pulse duration and intensity will be analyzed.
2. Summary of existing theories

Most existing theoretical methods that include simultaneously electronic and nuclear degrees of freedom have been applied to diatomic molecules. For this reason, this brief theoretical account is limited to this kind of molecules. The cases of stationary and time-dependent theories are discussed separately. For the former, interested readers are referred to two review articles [12, 13].

2.1. Stationary theories

2.1.1. Non resonant case. This is the usual approach when the photon-molecule interaction is well described within the lowest order of perturbation theory. For instance, in the case of one-photon ionization, the cross section is written, in the dipole approximation,

\[
\sigma_{\alpha v\alpha}(E) = \frac{4\pi^2 \omega}{3c} \sum_{\mu l m} \left| \int dR \langle \Psi_{iv}(r, R) | \vec{e}_p \cdot \vec{D} | \Psi_{\alpha v\alpha Ela,m}(r, R) \rangle \right|^2
\]  

(1)

where \( \alpha \) indicates the electronic state of the residual molecular ion and \( v_\alpha \) the corresponding vibrational (or dissociative) state, \( l_\alpha \) is the angular momentum of the ionized electron, \( m \) is the corresponding azimuthal quantum number, \( \Psi_{iv}(r, R) \) is the initial state, \( \Psi_{\alpha v\alpha Ela,m}(r, R) \) is the final state, \( r \) represents the electronic coordinates, \( R \) is the internuclear distance, \( \vec{D} \) is the dipole operator and \( \vec{e}_p \) is the photon polarization vector. The energy \( E \) is given by \( E = W_{iv} + h\omega \), where \( W_{iv} \) is the total energy of the molecule in the initial state and \( h\omega \) is the photon energy. Similarly, evaluation of multiphoton ionization cross sections, though based on different equations, requires the \( \Psi_{iv}(r, R) \) and \( \Psi_{\alpha v\alpha Ela,m}^+(r, R) \) states.

The practical problem is the evaluation of the \( \Psi_{\alpha v\alpha Ela,m}^+(r, R) \) continuum state. Early theoretical calculations of the molecular electronic continuum have been performed in the fixed-nuclei approximation. In this approximation, the positions of the two nuclei are fixed and, therefore, only electronic degrees of freedom are considered. Currently, the fixed-nuclei approximation, very often in combination with density functional theory for the description of the electronic continuum, provides a practical framework to study ionization of polyatomic molecules (see [13–15] and references therein). This is a reasonable approximation when one is not interested in the vibrational analysis of a molecular property (e.g., to evaluate total photo-absorption rates or total electron yields). However, even in this case, it may fail when the nuclei have enough time to move before ionization occurs.

The simplest description of a continuum state beyond the fixed-nuclei approximation is obtained within the Born-Oppenheimer (BO) approximation (for simplicity, rotational effects are neglected and the index \( m \) is not explicitly indicated in the following),

\[
\Psi_{\alpha v\alpha Ela}(r, R) \simeq \psi_{\alpha l\alpha \epsilon\alpha}(r, R) \chi_{v\alpha}(R) ,
\]

(2)

where \( \psi_{\alpha l\alpha \epsilon\alpha}(r, R) \) is the non resonant electron-molecular ion scattering wave function for different positions of the nuclei, \( R \), and which \( \chi_{v\alpha} \) is nuclear wave function of the molecular ion is the solution of the equation

\[
[T(R) + \mathcal{E}_\alpha(R) - W_{v\alpha}]\chi_{v\alpha}(R) = 0 ,
\]

(3)

where

\[
T(R) = -\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{J(J+1)}{2\mu R^2}
\]

(4)

with \( J \) the total angular momentum, \( \mathcal{E}_\alpha(R) \) is the BO potential energy curve of the residual ion, \( W_{v\alpha} \) is its total energy and

\[
E = \epsilon_\alpha + W_{v\alpha} .
\]

(5)
Equation (2) is often called, in the context of electron-molecule scattering theory, the \textit{adiabatic nuclei approximation} [16].

Thus, the main practical problem is the evaluation of the electron-scattering wave function \( \psi_{\alpha l_\alpha l_\alpha}^{0+}(r, R) \) for the case of a molecular ionic target. Notice that, in order to perform the integral over \( R \) in equation (1), this wave function must be obtained at different values of \( R \). Several accurate methods have been successfully developed to evaluate \( \psi_{\alpha l_\alpha l_\alpha}^{0+}(r, R) \). Among them, it is worth mentioning (i) the discretized close-coupling (DCC) method [12, 17–19] and the convergent close-coupling (CCC) method [20–22], in which the electronic wave function is written as a combination of products of target and scattering electronic wave functions with the appropriate boundary conditions, (ii) the exterior complex scaling (ECS) method [23–25], in which the electronic coordinates are scaled in the complex plane beyond a certain (usually large) distance \( r_0 \) thus ensuring the correct asymptotic behavior for \( r_i < r_0 \), and (iii) the R-matrix method (and its many extensions, see, e.g., [26–28] and references therein), in which the problem is first solved within a sphere of finite size and then the asymptotic behavior is switched on later from outside the sphere. In principle, all these methods can be implemented by using different basis sets and/or grid methods. Two of the most successful implementations make use of B-spline basis functions [13, 29] and the finite-difference DVR method [24].

2.1.2. Resonant case. As in atoms, the molecular electronic continuum may include resonances associated with multiply excited electronic states (Feshbach resonances) or electronic states with inner-shell vacancies. These are quasi-bound states that decay by autoionization, a process that is significantly slower than direct ionization (typically of the order of a few fs). There is, however, an important difference with the atomic case: in a molecule, autoionization can also lead to dissociation into neutral fragments [30]. This is due to the weakly-bound or repulsive character of the potential energy curves associated with molecular autoionizing states. Thus autoionization and dissociation may occur simultaneously leading to complicated interference phenomena as those observed in H\(_2\) and D\(_2\) photoionization experiments [31, 32]. It is thus clear that, in order to describe all possible ionization and dissociation pathways and the competition between them, the wave function cannot be written in the usual BO way as a simple product of an electronic function times a nuclear function.

The appropriate theoretical framework was initiated by Bardsley [33] and Hazi, Rescigno and Kurilla [34], and further developed by Sánchez and Martín [35–37]. In this case, the final state wave function \( \Psi_{\alpha v_\alpha v_\alpha}^{+}(r, R) \) is given by:

\[
\Psi_{\alpha v_\alpha v_\alpha}^{+}(r, R) = \sum_{l'\alpha'} \sum_{\alpha l_\alpha l_\alpha} \phi_{\alpha l_\alpha l_\alpha}(r, R) \xi_{\alpha v_\alpha v_\alpha}^{l'}(R) + \psi_{\alpha l_\alpha l_\alpha}^{0+}(r, R) \chi_{\alpha v_\alpha v_\alpha}(R) + \lim_{\eta \to 0} \sum_{l'\alpha'} \sum_{\alpha l_\alpha l_\alpha} \sum_{R} \int dE' \frac{1}{E - E' + i\eta} \int dR' V_{\alpha l_\alpha l_\alpha}^{r} E'(R') \xi_{\alpha v_\alpha v_\alpha}^{l'}(R) \chi_{\alpha v_\alpha v_\alpha}(R),
\]

where

\[
H_{el} = \langle \phi_\alpha | H_{el} | \psi_{\alpha l_\alpha l_\alpha}^{0+} \rangle \chi_{\alpha v_\alpha v_\alpha}(R),
\]

\( E - E_r(R) - T(R) \xi_{\alpha v_\alpha v_\alpha}^{l'}(R) = V_{\alpha l_\alpha l_\alpha}^{r} E(R) + \lim_{\eta \to 0} \sum_{l'\alpha'} \sum_{\alpha l_\alpha l_\alpha} \sum_{R} \int dE' \frac{V_{\alpha l_\alpha l_\alpha}^{r}}{E - E' + i\eta} \int dR' V_{\alpha l_\alpha l_\alpha}^{r} E'(R') \xi_{\alpha v_\alpha v_\alpha}^{l'}(R') \chi_{\alpha v_\alpha v_\alpha}(R').
\]
The symbol $\Sigma$ indicates a summation over bound states and an integral over continuum states. The latter equation represents the nuclear motion when the electrons are in the quasi-stationary state $\phi_r$. The matrix element in equation (7) represents the coupling between the resonance $\phi_r$ and the non resonant wave function $\psi_{\alpha_lr\alpha}^0$ and vibrational state $\chi_{\alpha l}$ (the modulus square of the bracket is proportional to the corresponding autoionization width). Hence, the two terms in the right-hand side of equation (8) are the result of the autoionizing character of the $\phi_r$ state. Notice that in the latter equations the electronic and nuclear wave functions are coupled, which is essential to describe the nuclear motion while the molecule autoionizes. This is not possible with the simple BO expression (2). A similar method has been used to study resonant effects in collisions of $\text{H}_2$ with fast highly charged ions [10] and electrons [38].

2.2. Time-dependent theories

Time-dependent methods are more appropriate when the interaction between the molecule and the radiation field occurs in a short time interval and/or when the intensity of the radiation field is high enough to invalidate the use of perturbation theory. Thus it is a method that is widely used to describe the interaction of molecules with (intense) ultrashort laser pulses. In this context, one has to solve the time-dependent Schrödinger equation (TDSE)

$$i\frac{\partial}{\partial t}\Phi(r, R, t) = [H + V(t)]\Phi(r, R, t)$$

where $H$ is the total hamiltonian of the molecule in the body-fixed frame and $V(t) = p \cdot A(t)$ is the laser-molecule interaction potential.

Several computational approaches have been successfully developed to solve this equation. Within the fixed-nuclei approximation, nearly exact numerical solutions of the TDSE have been reported for the $\text{H}_2^+$ molecular ion (see, e.g., [39–45] and references therein) and for $\text{H}_2$ [46–48]. Numerical solutions seeking to include the vibrational motion have only been obtained by reducing the dimensionality of the problem [49, 50]. Very recently, the full dimensionality of the electronic and vibrational problem has been taken into account by performing a close-coupling expansion of the time-dependent molecular wave function $\Phi(r, R, t)$ [51–60] (this is at variance with previous applications of the time-dependent close-coupling method within the fixed-nuclei approximation [61, 62]). In this method, $\Phi(r, R, t)$ is expanded in the basis of stationary vibronic states $\Psi_{\alpha l}(r, R)$ of energy $W_{\alpha l}$,

$$\Phi(r, R, t) = \sum_n \sum_\nu \psi_{\nu n}(r, R) e^{-iW_{\nu n}t} + \sum_{\alpha, \lambda} \int d\varepsilon \sum_{\nu \alpha} c^{\lambda\alpha}_{\nu \alpha\nu_\alpha}(t) \chi_{\alpha \lambda}(r) e^{-iW_{\nu \alpha\nu_\alpha}t},$$

where the first term is a summation over bound electronic states $n$ and their corresponding vibrational states $\nu$. The second term includes (i) a summation over different ionization limits $\alpha$, (ii) a summation over the angular momentum $l_\alpha$ of the ejected electron, (iii) an integral over electronic continuum states of energy $E_{\nu n}(R) = E_{\nu n} + \varepsilon_\alpha$ (with $E_{\nu n}(R)$ the potential energy curve of the ionization limit $\alpha$ and $\varepsilon_\alpha$ the energy of the ejected electron), and (iv) a summation over their corresponding bound vibrational states and an integral over continuum ones. Substituting (10) in (9) leads to a system of coupled differential equations, which are integrated to obtain the coefficients $c_{\nu n}(t)$ and $c^{\lambda\alpha}_{\nu \alpha\nu_\alpha}(t)$ at large enough $t$. The squares of the latter coefficients give the various differential probabilities of the process. It is important to stress here that, in all existing applications of the time-dependent close-coupling method, non adiabatic couplings associated with the derivatives of the electronic wave functions with respect to the nuclear coordinates that arise upon substitution of expansion (10) in the TDSE are partially or totally neglected. In this context, and for practical reasons, it is most convenient to write the molecular stationary states $\Psi^{\alpha \lambda}_{\nu \alpha\nu_\alpha}(r, R)$ in the BO form given by equation (2) [59]. A similar simple expression can be used
for autoionizing states provided that their coupling with the non resonant continuum states is also included (see [57] for details).

In the following, a sample of results obtained with the above mentioned theories will be discussed. Emphasis will be put on those results that have led to interesting new physical effects. All of them concern the H₂ or D₂ molecules.

3. Photoionization of H₂ at high photon energies

The first example is ionization of H₂ by photons of up to a few hundreds of eV. The typical size of diatomic molecules is given by their internuclear distance, \( R \), and is of the order of 1 Å in most cases (e.g., 0.74 Å for H₂ and 1.06 Å for H₂⁺). Therefore, interferences are expected to show up when the photon energy, \( h\nu \), is of the order of a hundred eV \( [h\nu \sim I_p + h^2/(2m_e\lambda_e^2)] \), where \( I_p \) is the vertical ionization potential. An indication of the interferences associated with fast electron emission can already be seen in the integral photoionization cross section, which approximately follows the formula \([63]\), \( \sigma_A \equiv [1 + \sin(k_e R)/ (k_e R)] \), where \( \sigma_A \) is the atomic photoionization cross section (for an effective charge \( Z_{eff} \)) and \( k_e = 2\pi/\lambda_e \) is the electron wave vector. The signature of interferences is, as usual, the oscillatory term within the brackets. However, due to the rapid decrease of \( \sigma_A \) with photon energy, i.e., with \( k_e \), oscillations are usually observed in a rather indirect way, e.g., by dividing the total cross section by a “reasonable” independent estimate of \( \sigma_A \) \([64,65]\) or by studying the ratio of two rapidly decreasing partial cross sections \([66]\).

Much clearer evidence of interferences can be obtained from fixed-in-space molecules. This was anticipated in 1969 by Kaplan and Markin \([67]\) and further investigated by Walter and Briggs \([68]\), who used a very simple model in which molecular orbitals are represented by a combination of two atomic orbitals, the continuum electron is described by a plane wave and the nuclei do not move. Experiments with fixed-in-space molecular orientations are now in progress and some results for electron impact ionization of H₂ are already available \([69]\).

Fig. 1 presents the results of recent theoretical calculations \([70]\) including the full dimensionality of the electronic and vibrational motions. Panels (a) show the integrated (in electron energy and solid angle) cross section as a function of photon energy for polarized light parallel (\( \Sigma_u^+ \) symmetry) and perpendicular (\( \Pi_u \) symmetry) to the molecular axis. Only the dominant non dissociative contribution (H₂⁺ (1s\( \sigma_g \)) + e⁻) is given. For the parallel arrangement (upper box) the different partial waves (denoted by \( l \)) exhibit pronounced minima at very specific photon energies. These minima lead to shallow dips in the total photoionization cross section. The first minimum appears when the electron wave vector satisfies \( k_e R \sim \pi/2 \). This formula describes momentum quantization of an electron moving inside a one-dimensional box of length \( R \), which suggests that the observed minima are due to electron confinement at a given internuclear distance. For the perpendicular II_u arrangement (panel (a) in the lower box of Fig. 1), a similar effect is not observed.

At a given photon energy, the electron wave length \( \lambda_e \) depends on the energy sharing between the ionized electron and the residual ion: \( \nu' + h\nu = W_{\nu'} + W_{\nu} = k^2/(2m_e\lambda_e^2) \). Panels (b) in Fig. 1 show the differential (in \( \lambda_e \) or equivalently in the energy of H₂⁺) cross sections and the contribution of the different partial waves for the photon energies indicated by vertical dashed lines in panel (a). In the \( \Sigma_u^+ \) case, the chosen photon energy is close to one of the relevant minima in the partial cross sections (i.e., where confinement is expected to occur). It can be seen that the relative contributions of the different partial waves depend on the energy of the ejected electron. This implies very different angular distributions for different energy sharings (see panel (c)) and the three dimensional polar plots. In the case of polarized light parallel to the molecular axis (top of Fig. 1), the angular distribution of the fastest electrons (i.e., of those electrons associated with a residual H₂⁺ ion in a low vibrational state) exhibits an almost perfect f shape (\( l = 3 \)). As we consider slower and slower electrons (i.e., H₂⁺ in higher vibrational states), the \( l = 1 \) and \( l = 3 \) waves interfere leading to a complicated angular pattern, until \( l = 1 \) dominates and an almost...
pure p wave is found. These variations in the electron angular distribution are also responsible for the non Franck-Condon vibrational distribution of the residual $H_2^+$ ion (a Franck-Condon distribution decreases much faster with $v$).

When the polarization is perpendicular to the molecular axis ($\Pi_u$ symmetry shown in the lower box of Fig. 1), the angular distribution is quite different: a dominant lobe appears along the polarization direction accompanied by smaller lobes on each side. The calculated angular distributions remind us of the interference patterns observed in Young’s double-slit experiment.

4. Double photoionization of $H_2$

Experiments in which both electrons are ejected from an oriented hydrogen molecule by absorption of a single photon are currently available [9, 71–73]. Among the latter, Weber et al. [9, 72] have recently demonstrated that the ejection pattern of the electrons depends sensitively
Figure 2. (Colour on line) Angular distribution (TDCS) of ejected electrons with direction of one electron (red arrow) with 90% of the available energy fixed along the polarization direction (green arrow) at three values of the internuclear distance and for a photon energy of 75 eV.

on the bond distance between the two nuclei as they vibrate in their ground state. In the experiments, linearly polarized 75 eV synchrotron radiation was used to study single-photon induced fragmentation of molecular deuterium. By measuring the final momenta of both nuclei and the ejected electrons in coincidence, they were able to relate the angular pattern of the ejected electrons to a particular internuclear separation in the molecular ground state at the instant of photon absorption. The experimental results showed that this essentially classical interpretation of nuclear motion (consistent with the "reflection principle" for photodissociation spectra) is valid for the conditions of the experiment. Recent theoretical work has reported the first complete numerical solution of the Schrödinger equation for the double photoionization of H$_2$ [25, 47, 74–76]. The results have shown that the distribution of photoelectrons emitted from aligned molecules reflects electron correlation effects that are purely molecular in origin. Figure 2 shows the triply differential cross section (TDCS) at three internuclear distances: the equilibrium position of the nuclei and the inner and outer classical turning points of their vibrational motion in the ground vibrational state.

Fig. 3 shows the comparison of those calculations, averaged over the experimental acceptance ranges, with the experimental results at a photon energy of 75 eV and equal energy sharing for the two ejected electrons. This comparison verifies a key result of the experiments, namely an apparent rotation in the emission pattern of ejected electrons as the bond distance varies. The effect is most apparent in the full 3D plots. As Weber et al. [72] point out, in the analogous atomic case of helium the light field apparently drives electrons towards a dipole pattern keyed to the axis of polarization, whereas in the geometry of the experiment shown in Fig. 3 the molecule emits the in-plane electron strongly perpendicular to its axis. As the molecule is stretched that effect becomes more pronounced. Why does the fully differential cross section rotate with changing internuclear distance? This cross section is a coherent sum of contributions to the double photoionization amplitude from the components of the polarization parallel ($\Sigma_u$) and perpendicular ($\Pi_u$) to the molecular axis [75]. As shown in [76], the parallel contribution has a minimum in the range of internuclear distances being sampled by the experiment, while the perpendicular one decreases monotonically as $R$ increases. It is these different variations that are responsible for the rotation of the cross section with changing $R$. 

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Figure 3. (Colour on line) Angular distributions for the case of equal energy sharing between the two electrons. The fixed electron (single arrow) is perpendicular to the plane formed by the molecule (violet) and the polarization (vertical double arrow). The molecule is aligned at 55° to the polarization. The results (left to right) are for kinetic energy releases of 0.50–0.60, 0.65–0.75, and 0.75–0.85 hartrees, respectively. Top: comparison with the relative experimental results (points) of [9, 72]. The theoretical results (solid lines) are integrated over the finite ranges of electron ejection angles, energy sharings and molecular orientations of the experiment. Bottom: corresponding full 3D distributions for KER of 0.55, 0.70, and 0.80 a.u., not integrated over any experimental acceptance ranges.

5. Photoionization of H₂ through autoionizing states

Doubly exited states and their decay give rise to the multitude of narrow structures, called Fano resonances [77], in atomic photoionization spectra. These structures are the result of interference between two indistinguishable pathways through which the electron can be ejected. The photon can either expel an electron directly, or else promote the atom to a doubly excited state, which then decays after a delay by emission of one electron via autoionization. Because the final state in both of these pathways is the same, the amplitudes for each pathway must be added coherently, leading either to constructive or destructive interference, depending on the phase shift induced by the time delay. Doubly excited states have also been seen [31, 32, 78, 79] and predicted ([37, 80] and references therein) for molecules. Because in molecules the excess photon energy can be distributed among internal nuclear and electron degrees of freedom however, the situation is much more complex than in atoms, and a clearcut proof of the interference effects is missing.

In a very recent work [11], it has been clearly demonstrated that such interference effects cause symmetry breaking in dissociative photoionization. A first observation of asymmetric photoelectron emission from H₂ has been reported in pioneering experiments by Lafosse et al. [81]. In a different context, asymmetric electron emission has also been observed in O₂ [82] as the result of the decay of atomic oxygen following photodissociation of the O₂ molecule. In this case, the observed asymmetry thus does not strictly arise from a molecular decay process.

Figure 4 shows the kinetic energy release (KER) distribution for dissociative ionization as a function of the photon energy. Three areas with islands can be distinguished (I, II and III in Fig. 4b): region I and III can be populated by direct ionization, leaving H⁺ in the 2π_u or 1σ_g state, respectively. However, only the latter state contributes significantly, as a direct dipole
transition from the H$_2$ ground state to the 2p$_\sigma_u$kπ$_g$ continuum is very unlikely [37] (in fact, it would be strictly forbidden in an independent electron picture). Thus regions I and II cannot be the result of a single-step direct photoionization. They are the fingerprint of a delayed emission of an Auger electron from H$_2$ doubly excited states (either Q$_1$ or Q$_2$ [11]). These states can either dissociate due to the repulsive character of the corresponding potential energy curve or decay by autoionization into the 2p$_\sigma_u$ or 1s$_\sigma_g$ states when such a decay is faster than the time required for an effective dissociation. Thus the five pathways contributing to ionization in the photon energy range of figure 4 are

\begin{align}
  h\nu + H_2 &\rightarrow H^+_2(1s_\sigma_g) + e^- , \quad \text{direct} \tag{11} \\
  h\nu + H_2 &\rightarrow H^+_2(2p_\sigma_u) + e^- , \quad \text{direct} \tag{12} \\
  h\nu + H_2 &\rightarrow H_2(Q_1) \rightarrow H^+_2(1s_\sigma_g) + e^- , \quad \text{resonant} \tag{13} \\
  h\nu + H_2 &\rightarrow H_2(Q_2) \rightarrow H^+_2(1s_\sigma_g) + e^- , \quad \text{resonant} \tag{14} \\
  h\nu + H_2 &\rightarrow H_2(Q_2) \rightarrow H^+_2(2p_\sigma_u) + e^- , \quad \text{resonant} \tag{15}
\end{align}

Asymptotically, H$_2^+(2p_\sigma_u)$ always leads to dissociation, whereas H$_2^+(1s_\sigma_g)$ can lead either to H$_2^+$ in a bound vibrational state or to a dissociative state. All these pathways must be added coherently if they yield the same electron energy and hence the same KER. Their interference leads to the distinct finger-like structures in the low KER region (Fig. 4c-f). The calculated structures (Fig. 4c,e) are in excellent agreement with the experimental observations (Fig. 4d,f). The calculations show that the structure is the result of an interference between the processes in eqs. (11) and (13), the direct and resonant pathways leading to 1s$_\sigma_g$ in the same KER region.
Figure 5. (Colour on line) Angular distribution of the electrons as a function of KER for dissociative ionization of D$_2$ at a photon energy of 33.25 eV, linearly polarized light. The angle-integrated KER spectrum is shown at the bottom (red line: theory, black line: experiment; letters a to f correspond to the six labelled spectra above; KER intervals: ±0.1eV). The orientation of the molecule at 90° to the polarization (theory) and 90±10° (experiment) is indicated by colored circles (blue = deuteron, green = deuterium). The (horizontal) polarization vector and the molecular axis define a common plane. The electron is restricted to this plane by ±45°. Full red line: theory, circles with error bars: experiment, dotted line: fit of the experimental data with spherical harmonics. The theoretical results have been integrated over the experimental acceptance angles and KER resolution as well as electron resolution. Infinite resolution theoretical results are shown by the small three-dimensional plots in the upper right: KER = 0.2 (a), 6.3 (b), 7.8 (c), 9.2 (d), 11 (e), and 14 eV (f).

The finger-like structures are the molecular analogue of the well-known Fano interferences in the atomic case, but there are important differences due to the molecular character of H$_2$.

Figure 5 shows the the angular distribution of the electron with respect to the polarization axis (horizontal). The plane of the figure is defined by the molecular axis and the polarization vector; only electrons in this plane are selected. The molecule is perpendicular to the polarization axis with the proton pointing upwards. The angular distributions vary strongly with the kinetic energy release. Besides a change from a dumbbell to a butterfly shape, a strong asymmetry is found, in particular in a narrow range of KER ≃ 8-10 eV, corresponding to an electron energy of $E_e \approx$ 5-7 eV. All major features predicted by theory are confirmed by the experiment.

The analysis of the calculations reported in [11] allows one to distinguish the contributions leading to 1$s\sigma_g$ [sum of processes in eqs. (11), (13) and (14)] from those leading to 2$p\sigma_u$ (sum of processes in eqs. (12) and (15)). For a fixed photon energy of 33.25 eV, the contributions of the 1$s\sigma_g$ and 2$p\sigma_u$ channels overlap in the 8-10 eV region, where the largest asymmetry is observed (Fig. 5). The asymmetric angular distribution results from the interference between the 1$s\sigma_g$ and 2$p\sigma_u$ ionization channels. This has been proved by model calculations [11] in which only the
decay of the lowest $Q_2$ autoionizing state of $^1\Pi_u$ symmetry through the $1s\sigma_g$ and $2p\sigma_u$ channels [eqs. (14) and (15)] was included. Even in this simplified model, the asymmetry remains, thus showing that the origin of the asymmetry is the interference between these two channels, i.e., between the resonant population of an ungerade and a gerade state. It is only the coherent superposition of these pathways which allows for a localization of the bound electron in the dissociating $H_2^+$. The transient molecule has broken symmetry and can keep a memory of the direction in which the electron departed.

Asymmetric photoelectron angular distributions should arise in any symmetric molecule that decays through two (or more) dissociative ionization channels associated with different symmetries of the residual molecular ion. When the final electron energy is the same in both channels, the corresponding ionization pathways are indistinguishable. This equivalence leads to interferences that depend on the time delay between the two ionization processes. The time delay implies that the decay in either pathway occurs at different positions of the nuclei. This unique relationship between time delay and nuclear positions makes the problem of molecular autoionization much richer than the atomic case, with the asymmetry of the photoelectron angular distribution the most striking effect.

6. Ionization of $H_2$ by ultrashort vuv laser pulses

So far most experimental studies of ionization of molecules by ultrashort pulses have made use of the Ti:sapphire laser at $\sim 800$ nm central wavelength [83–92]. For this wavelength, ionization requires the absorption of many photons, which makes the process highly non perturbative even at relatively low intensities (e.g., $10^{12}$ W/cm$^2$). Thus most theoretical approaches used to interpret these experiments are based on high-field models, like the ADK model [84,93], simplified Floquet approaches [94], or reduced time-dependent calculations [95]. In contrast, the production of fs and sub-fs, vuv and xuv laser pulses by means of high-order harmonic generation [96–98] or free electron lasers [99–101] has opened up the way to investigate simpler two- and three-photon ionization processes in $H_2^+$ and $H_2$ by solving the TDSE. Such ultrashort pulses are also ideal to investigate physical problems at the atomic and molecular time scales. Indeed, the dynamics of bound electronic states typically occurs in the sub-fs time scale (the revolution time of an electron orbiting around a proton is $\sim 150$ attoseconds) and that of autoionizing states, although generally much slower, occurs in the fs time scale. Recent experiments on rare gas atoms have taken advantage of this fact to provide interesting temporal pictures of ionization [97,102,103] and autoionization [103].

The nuclear motion in molecules occurs in the fs time scale and, therefore, may compete efficiently with slow electronic processes such as autoionization [35,37]. Thus the use of vuv and xuv/fs pulses allows one to explore the possibility of controlling molecular dissociation and ionization [104]. In ref. [54] it has been shown that inclusion of the nuclear degrees of freedom in the description of $H_2$ ionization by vuv/fs laser pulses has a dramatic effect in resonance enhanced multiphoton ionization (REMPI): the latter can be several orders of magnitude larger than predicted by the fixed nuclei approximation. It has also been shown [54] that the relative importance of dissociative vs non dissociative ionization can be controlled by varying the pulse duration at a moderate intensity ($I = 10^{12}$ Wcm$^{-2}$). This is illustrated in Fig. 6 where the variation of the dissociative and non dissociative probabilities with pulse duration is shown for a fixed photon energy of 0.49 a.u.. It can be seen that both probabilities vary with pulse duration in a monotonous way and that the dissociative ionization probability increases by more than two orders of magnitude when the pulse duration is varied from 2 to 12 fs. As Fig. 6 shows, the results are practically the same for different pulse envelopes and phases, which is not surprising because vuv/fs pulses contain a large number of cycles.

Another interesting effect is observed when the pulse intensity is increased. Figure 7 shows the vibrational distribution of $H_2$ molecules remaining in the $B^1\Sigma_u^+$ and $B'1\Sigma_u^+$ excited states
Figure 6. (Colour on line) Variation of dissociative and non-dissociative ionization probabilities with pulse duration at a fixed photon energy $\omega = 0.49$ a.u. and intensity $I = 10^{12}$ W cm$^{-2}$. Full lines: cosine envelop; circles: gaussian envelop with the same full width at half maximum (FWHM); triangles: gaussian envelop with the same integral. All previous results obtained with $\phi = 0$. Squares: cosine envelop and $\phi = \pi$; crosses: cosine envelop and $\phi = \pi/2$.

for pulses of 5 fs and $\omega = 0.46$ a.u.. At the lowest intensity ($10^{13}$ W cm$^{-2}$), the width of the $B^{1}\Sigma_{u}^{+}$ vibrational distribution reflects more or less the bandwidth of the pulse (0.06 a.u.). As the intensity increases, higher and higher vibrational levels of the upper $B^{1}\Sigma_{u}^{+}$ state are populated. This is the consequence of a step ladder mechanism associated with Rabi-type oscillations between the $X^{1}\Sigma_{g}^{+}$ and $B^{1}\Sigma_{u}^{+}$ states (see Fig. 8 and references [55, 59]). The mechanism is illustrated in Fig. 9: in the first half of the first Rabi oscillation, a band of $B^{1}\Sigma_{u}^{+}$ vibrational states is populated; then, in the second half of the oscillation, the population goes back to the $X^{1}\Sigma_{g}^{+}$ electronic state, but this time not only to the $v = 0$ but also to the $v = 1$ (and 2) vibrational states (because the bandwidth $\Delta \omega$ is larger than the corresponding vibrational spacing, see also Fig. 8); thus, in the first half of the second oscillation, the photon can be absorbed from the excited $v = 1$ level of the $X^{1}\Sigma_{g}^{+}$ electronic state and, as a consequence, higher electronic states are reached. In other words, the step ladder mechanism gives access to intermediate electronic states that are not accessible by direct single photon absorption. Fig. 9 shows that the amplitude of the oscillations decreases with time, which reminds one the damping of Rabi oscillations in a two-level system when the upper level has a width (in this case, due to photoionization). Interestingly, Fig. 7 shows that, as the intensity increases, two peaks appear, which can be interpreted as resulting from the Autler-Townes splitting between the dressed $X^{1}\Sigma_{g}^{+}$ and $B^{1}\Sigma_{u}^{+}$ electronic states (see Fig. 8).

7. Concluding remarks
This manuscript has presented an overview of the theoretical methods developed in recent years to simultaneously describe molecular ionization and dissociation induced by synchrotron radiation and ultrashort laser pulses. These methods have already provided accurate results
Figure 8. (Colour on line) The relevant potential energy curves of H$_2$. A typical (1+1) resonant transition leading to ionization is shown. Rabi oscillations are indicated by a double arrow. The Autler-Townes splitting for a pulse of 10 fs and 2×10$^{14}$ W cm$^{-2}$ is also shown.

for the simplest H$_2^+$ and H$_2$ molecular systems, and are expected to do a similar job for other diatomic molecules. In particular, the good agreement achieved between theoretical predictions and measurements obtained in kinematically complete experiments is remarkable, even for fully differential angular distributions and even more for the double ionization process. The success of these theories relies on their ability to simultaneously account for electronic and vibrational degrees in their full dimensionality. This is essential, e.g., to correctly describe resonance effects in which the ionization process occurs in a time scale comparable to that of the molecular vibrations. Inclusion of the additional rotational degrees of freedom in the near future should be straightforward.

All this work has led to a much better understanding of molecular ionization and, in particular, of the complicated interference effects that arise when dissociative channels are accessible. New, sometimes unexpected physical phenomena have been discovered and explained, such as electron confinement for wavelengths of the order of the molecular size, the strong variation with internuclear distance of the electron angular distribution in double ionization, the possibility of breaking the symmetry of the electron angular distribution in homonuclear systems when autoionization competes efficiently with direct ionization, the control of molecular dissociation processes by using laser pulses of different duration and intensity, and the existence of step-ladder Rabi oscillations when intense vuv/fs laser pulses are used in molecular systems. By the end of the twentieth century, many of these effects were suspected to occur, but the final theoretical and experimental proof has only been given very recently.

In spite of this progress, we are still far from being able to describe ionization of polyatomic molecules with a similar high degree of accuracy. In this case, the existence of several vibrational modes makes the problem much more difficult, not only because this implies more degrees of freedom, but also because the different vibrational modes can be coupled. Many theoretical studies reported so far are based on the fixed nuclei approximation or on extensions of the latter
approximation by using Franck-Condon weights. However, it has been known for a long time that inclusion of the nuclear motion is extremely relevant to understand ionization spectra of polyatomic molecules even qualitatively. In particular, the presence of conical intersections is widespread and dominate the appearance of ionization spectra [105]. Thus accurate methods to compute the nuclear quantum dynamics in systems with up to 20-30 degrees of freedom have already been developed (see e.g. the review [106]), but the interplay with the electron dynamics still relies on important simplifications such as the local approximation [107, 108]. Therefore the challenge for the next few years is to go beyond these approximations in polyatomic molecules, which will lead to a better understanding of the role of dissociative ionization processes in such complex systems.

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