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ELECTRON ANGULAR DISTRIBUTIONS IN DISSOCIATIVE PHOTOIONIZATION OF THE HYDROGEN MOLECULE

DISTRIBUCIONES ANGULARES ELECTRÓNICAS EN LA FOTOIONIZACIÓN DISOCIATIVA DE LA MOLÉCULA DE HIDRÓGENO

DISTRIBUIÇÕES ANGULARES DE ELÉTRONS NA FOTOIONIZAÇAO DISSOCIATIVA DA MOLÉCULA DE HIDROGÊNIO

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ABSTRACT

A method to calculate angular distributions for electrons ejected from fixed-in-space molecular hydrogen molecules subject to ultrashort intense laser pulses is proposed, based on the ab initio solution of the time-dependent Schrödinger equation. This method of solution allows for a temporal picture of interferences arising in the dissociative ionization channel (in the proton kinetic energy spectrum) due to the presence of the autoionizing double excited states in the Hydrogen molecule. In particular, we show how this autoionization during the dissociative photoionization process may also induce a counterintuitive asymmetry in the angular distribution of the ionized electron with respect to nuclei inversion, in spite of dealing with an homonuclear system.

RESUMEN

Se propone un método para calcular distribuciones angulares de electrones ionizados en la molécula de hidrógeno fija en el espacio sometida a pulsos láser intensos y ultracortos, basado en la solución desde primeros principios de la ecuación de Schrödinger dependiente del tiempo. Esta solución nos permite tener una visión temporal de la interferencias generadas en el canal de ionización disociativa (en el espectro de energía cinética de los protones) debido a la presencia de la autoionización de estados doblemente excitados de la molécula de hidrógeno. Se muestra específicamente cómo la autoio-

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nización durante el proceso de fotoioniza-ición disociativa también puede inducir una asimetría en la distribución angular del electrón ionizado con respecto a la inversión nuclear, un efecto no intuitivo a pesar de estar tratando con un sistema homonuclear.

Palabras clave: cálculos ab initio, molécula de hidrógeno, fotoionización molecular, distribuciones angulares electrónicas.
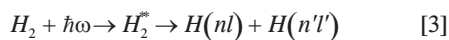
RESUMO

Propõe-se um método para calcular as distribuições angulares de elétrons ioni-zados de uma molécula de hidrogênio fixa no espaço, sujeita a pulsos de laser inten-sos e ultra-curtos, baseado na soluçao desde primeiros princípios da equaçao de Schrödinger dependente do tempo. Esta soluçao nos permite ter uma visão tempo-ral das interferências geradas no canal de ionizaçao dissociativa (no espectro de energia cinética dos prótons) devido á presença da auto-ionização de estados du-plamente excitados da molécula de hi-drogênio. Mostra-se especificamente como a auto-ionização durante o processo de foto-ionização dissociativa pode tam-bém induzir uma assimetria na distribuiç-ão angular do elétron ionizado com res-peito á inversão nuclear, um efeito não intuitivo apesar de estar se tratando de um sistema homonuclear.

Palavras-chave: cálculos ab initio, molécula de hidrogênio, fotoionização molecular, distribuições angulares eletr-ônicas.

INTRODUCTION

For decades the main concern of quantum chemistry has been the development of methodologies to calculate ab initio bin-ding energies and stable geometrical structures from simple to complex mole-cules, mostly in their ground state. In dealing with chemical reactivity, quan-tum chemistry also begins to envisage models and methods for dynamical pro-cesses in which not only the ground state but also excited states are involved in the reaction mechanisms. In particular, when molecules are subject to radiation, one opens the way to multichannel reaction phenomena which is the area of study of photochemistry. Nevertheless, even for simple molecules, the processes appea-ring in laser-molecule interactions may be quite involved indeed and it is quite de-sirable to have a detailed temporal picture of reactions. In this work we study the io-nization photo dynamics of the hydrogen molecule H_2 subject to intense ultra short laser pulses with a quantum time-depen-dent method, specifically when the pho-ton energy takes the molecule to the re-gion where doubly excited states lie above two ionization thresholds. At va-riance with atoms, the absorbed photon energy is shared between electronic and nuclear degrees of freedom, so that the residual molecular ion H_2^+ may be left vi-brationally excited or in a dissociative state. Keeping the scheme as simple as possible, the reactions of H_2 under a laser radiation with photon energies above $\sim$ 23 eV may be summarized as follows:

$$H_2 + \hbar\omega \rightarrow H(nl) + H^+ + e^- \qquad [1]$$

$$H_2 + \hbar\omega \rightarrow H_2^+ + e^- \qquad [2]$$

$$H_2 + \hbar\omega \rightarrow H_2^{**} \rightarrow H(nl) + H(n'l') \qquad [3]$$

i.e., dissociative ionization [1], non dissociative ionization [2], and the last reaction [3] denotes that dissociation into neutrals which is only mediated by previously populated double excited states H_2^{**}. These superexcited states are called Q_1 resonances (lying above the $H_2^+(1\sigma_g)$ ionization threshold), Q_2 resonances (above the $H_2^+(2p\sigma_u)$ limit) and so on (see Figure 1). Since these states are immersed into an electronic continuum, they are metastable, a short lifetime in the scale of femtoseconds (fs) is associated to them and after being populated, they autoionize to produce also dissociative ionization [1] or non dissociative ionization [2], which implies a strong interference with the direct absorption reaction. Only those molecules that survive without being autoionized follow the dissociative path to produce excited hydrogen atoms $H(nl)$ [3]. The imprint of the key role that resonant states play in the photo dynamics may be directly appreciated in the distributions of the kinetic energy of protons released after molecular dissociation in reaction [1] and also in the production of atomic excited states $H(nl)$, which eventually decay radiatively. Both events were the subject of recent measurements. Ito *et al*. (1) measured kinetic energy distributions of the ejected H^+ at different photon energies and J.D. Bozek *et al*. (2) measured the production of Lyman α and Balmer α fluorescence from $H(nl)$ after photodissociation of H_2. A sophisticated time dependent theoretical, method to deal with such photoprocesses in H_2 has already been developed by, our group (3) and it reproduces the experimental data fairly well (2, 3, 4).

With the recent advent of COLTRIMS spectroscopic techniques (5), kinematically complete experiments, where the momenta of all charged particles is determined at each single event, are becoming available and now they represent a challenge to the theorist. In particular, for the dissociative ionization process [1], the experiment is able to determine the orientation of the hydrogen molecule at the time of electron ejection by photon impact. Since the orientation at a given time is known, one may claim that the electron came from a fixed-in-space mo-
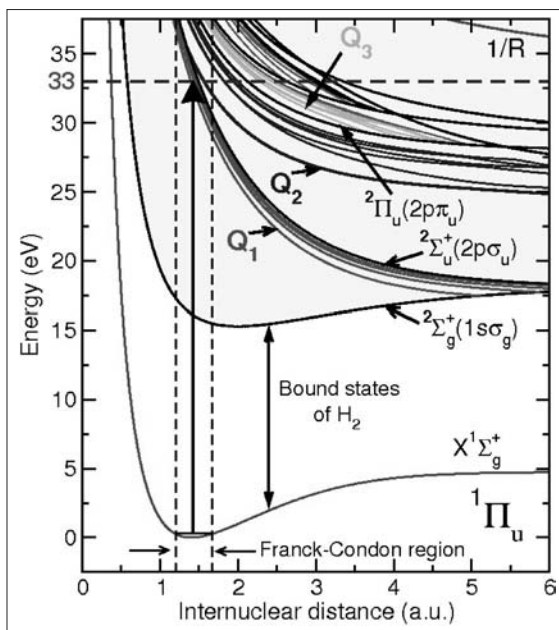

Figure 1. Potential energy curves of H_2 and H_2^+. The lowest two series of Q_1 and Q_2 autoionizing doubly excited states of H_2 with $^1\Pi_u$ symmetry are included. The vertical arrow indicates a one-photon transition of 33 eV from the ground state energy level within the Frank-Condon region.

lecule. Therefore, we develop a procedure to compute such angular distributions for the ionized photoelectrons and, since electronic and nuclear motions are coupled, we show their explicit dependence on the proton kinetic energy release.

METHOD OF SOLUTION

Our method is based on the solution of the time dependent Schrödinger equation (TDSE), which is appropriate when the laser-molecule interaction happens to occur in the time scale of atto- and femtoseconds (fs) and the laser intensity is large enough to invalidate perturbative approaches. Thus we solve the TDSE for the hydrogen molecule,

$$\left[H^0 + V(t) - i\frac{\partial}{\partial t} \right]\Phi(r,R,t) = 0 \qquad [4]$$

where H^0 is the field-free Hamiltonian of H_2 in the body-fixed frame and $V(t) = p\,A(t)$ represents the field interaction potential in the velocity gauge. A cosine-square modulated pulse with photon energy ω and duration T is switched on/off in the interval $[0, T]$. We then perform a close-coupling expansion of the time-dependent molecular wave function:

$$\Phi(r,R,t) = C_{gv_g}(t)\,\phi_g\chi_{v_g}e^{-iW_{gv_g}t}$$
$$+ \sum_{\alpha l_\alpha}\int d\varepsilon\sum_{v_\alpha}C_{\varepsilon_\alpha v_\alpha}^{l_\alpha}(t)\phi_{\varepsilon_\alpha}^{l_\alpha}\chi_{v_\alpha}e^{-iW_{\varepsilon_\alpha v_\alpha}t} \qquad [5]$$
$$+ \sum_{r}\sum_{v_r}C_{rv_r}(t)\phi_r\chi_{v_r}e^{-iW_{rv_r}t}$$

in terms of vibronic (electronic ϕ and nuclear χ) states of the ground g, continuum for each channel α with energy ε_α and angular momentum l_α of the ionized electron, and resonant states r of H_2. By inserting this expansion into the TDSE, a set of coupled differential equations is obtained

and solved numerically from time $t = 0$ (when the laser pulse starts) up to a time $t > T$ when the pulse is already gone. To compute total energies $W_{n,v}$ and electronic and vibrational wave functions included in [5] we cannot rely on the plethora of standard computational codes available for the theoretical chemist. In particular, the calculation of resonant and continuum states of molecules are still a no man's land in standard chemical computations, so that one has to tailor his own computer codes. The ground state of H_2 is evaluated by expanding the electronic wave function ϕ_g in a basis of configurations built from H_2^+ orbitals, which are represented in a one-center expansion in terms of B-splines basis within a radial box. The continuum wave functions $\phi_{\varepsilon_\alpha}^{l_\alpha}$ are calculated using a L^2 close-coupling method by using the same set of H_2^+ orbitals but with a well-defined angular momentum l for the escaping electron, which ensures that correct boundary conditions are imposed. The series of Q_n resonant states are obtained from the QH^0Q Feshbach-projected electronic Hamiltonian, with a configuration interaction method too. Vibrational wave functions were also computed in terms of B-splines basis for each electronic state. For further details the reader is referred to Ref. (3).

The ionization cross section, $W_{\varepsilon_\alpha v_\alpha}$ differential in the energy, for one photon absorption is computed from the coefficients $C_{\varepsilon_\alpha v_\alpha}^{l_\alpha}(t)$ for $t > T$ with the expression:

$$\frac{d\sigma}{dW_{v_\alpha}}\left(\frac{cm^2}{eV}\right) = \frac{8\omega}{3TI}\sum_{l_\alpha}\int d\varepsilon_\alpha\left|C_{\varepsilon_\alpha v_\alpha}^{l_\alpha}\right|^2 \qquad [6]$$

where the photon energy ω is given in Joules, the laser intensity I in W/cm^2 and the laser duration T in seconds. In order

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to compute electron angular distributions in the ionization channel, the final wave function [5] at time t > T must be projected onto the asymptotic incoming wave function (expanded in partial waves) that represents a free electron with energy ε_α plus a residual ion H_2^+ left in channel α. After some algebra, one arrives to the following expression for the density of probability differential in both proton kinetic energy E_{H+} and the solid angle Ω for the ejected electron:

$$\frac{d^2P}{dE_{H^+}d\Omega} = \int d\varepsilon \left| \sum_{\alpha l_\alpha m} i^{-l_\alpha} e^{i\delta_{l_\alpha}} Y_{l_\alpha m}^*(\Omega) C_{\varepsilon_\alpha v_\alpha}^{l_\alpha m} \right|^2 \quad [7]$$

where δ_{l_α} corresponds to the Coulomb phase shift. Short-range phase shifts are already included in the coefficients $C_{\varepsilon_\alpha v_\alpha}^{l_\alpha m}$ during the propagation. Note also that for dissociative ionization, $W_{\varepsilon_\alpha v_\alpha}$ is related to the center-of- mass energy of the ejected protons, $E_{H^+} = W_{\varepsilon_\alpha v_\alpha} - E_\alpha^\infty$ where E_α^∞ is the asymptotic energy of an H atom separated from an H^+ for the channel α.

RESULTS

To illustrate the performance of our method we provide results for the dissociative ionization of H_2 subject to a laser pulse with a photon energy of $\omega = 33$ eV, intensity $I = 10^{12}$ W/cm^2 and pulse duration $T = 10$ fs, perpendicularly polarized to the internuclear axis. Dipole selection rules imply that only the $^1\Sigma_g \rightarrow {}^1\Pi_u$ transition takes place. At this photon energy the ground state is excited to the Q_2 series of resonances (see Figure 1) along with the underlying two nonresonant continua corresponding to the open channels $H_2^+(1s_g)+e(\varepsilon l)$ and $H_2^+(2p\sigma_u)+e(\varepsilon l)$. Figure 2 shows the kinetic energy distri-

butions (KED) for the final $^1\Pi_u$ continuum calculated following (6) at photon energy $\omega = 33$ eV and pulse duration T = 10 fs, with separate contributions from $H_2^+(1s_g)$ and $H_2^+(2p\sigma_u)$ thresholds and it is compared with the experimental results by Ito et ál. (1), for protons observed at 90° with respect to the field polarization axis. The peaks structure in the KED for $1s\sigma_g$ and $2p\sigma_u$ curves only appears due to the presence of the autoionization of the Q_1 and Q_2 resonances, that produces $H_2^+(1s_g)+e(\varepsilon l)$ (both Q_1 and Q_2) and $H_2^+(2p\sigma_u)+e(\varepsilon l)$ (only Q_2). Closing the autoionization pathway, one should obtain simple Frank-Condon absorption profiles without peaks structure.

The origin of asymmetric electron angular distributions is attributed to the Q_2 autoionization decay into the two open channels mentioned above and the due interference between these two pathways. To satisfy the final $^1\Pi_u$ symmetry, the angular momentum for the emitted electron must be l = 1,3,5,... (p-,f-,.. *ungerade* waves) for the $H_2^+(2s_g)$ *gerade* threshold, and l=2,4,... (d-,g-,.. *gerade* waves) for the $H_2^+(2p\sigma_u)$ *ungerade* threshold. Electron angular distributions included in Figure 3 are taken at proton kinetic energies 2.31 eV, 4.16 eV and 6.46 eV and when the residual ion is left either in the $H_2^+(1s_g)$ state or in the $H_2^+(2p\sigma_u)$ state. At 2.31 eV, for instance, the $1s\sigma_g$ case clearly shows a dominant contribution of the *p*-wave and the $2p\sigma_u$, of a *d*-wave. One observes that these distributions are fully symmetrical with respect to nuclei inversion. However, molecular states as built in the LCAO model of the chemical bond dissociate into a mixture of atomic orbitals, i.e., $1s\sigma_g \rightarrow [1s_A + 1s_B]/\sqrt{2}$ and
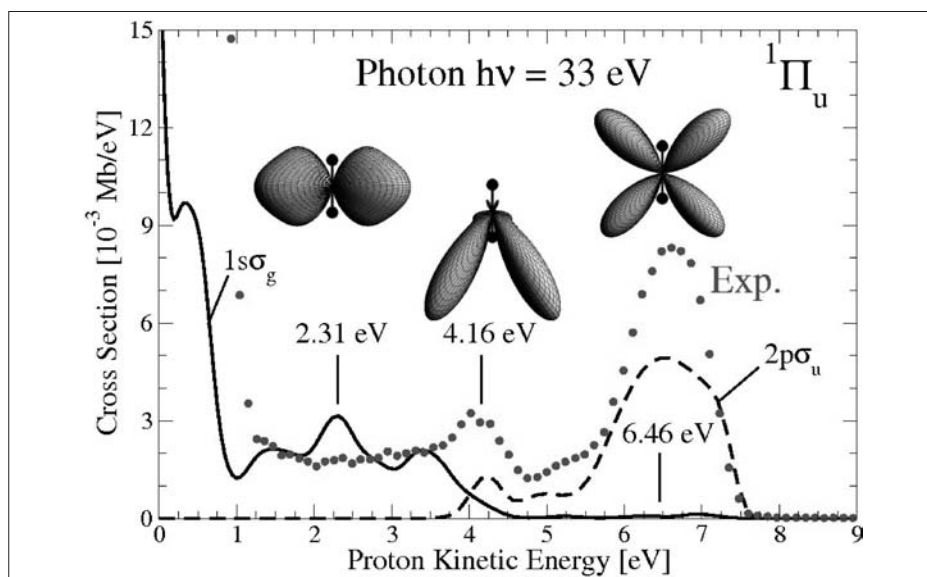
Figure 2. $^1\Pi_u$ proton kinetic energy distribution (KED) in the dissociative ionization of H_2 for protons detected at 90° with respect to the laser polarization axis and photon energy 33 eV. Solid line: contribution from the $^2\Sigma_g^+(1s\sigma_g)$ ionization channel; dashed line: contribution from the $^2\Sigma_u^+(2p\sigma_u)$ ionization channel; dots: experimental data from Ref. [1] must be compared with the sum of both contributions. Correct electron angular distributions (EADs) are in display for three selected proton energies. In the EADs the laser polarization vector is perpendicular to the molecular axis within the plane of the figures and the proton is pointing upwards. Mb stands for Megabarn (1 barn = 1024 cm^2).

$2p\sigma_u \rightarrow [1s_A - 1s_B]/\sqrt{2}$. These delocalized molecular orbitals are not truly connected with what one expects from a COLTRIMS experiment. Asymptotically, any experimental device will measure a localized electron bound in an H atom in a well-defined atomic state H(*nl*) plus a proton, a picture not provided by *gerade* or *ungerade* states. Accordingly, we must then project the total wave function onto the correct $1s_A \sim 1s\sigma_g + 2p\sigma_u$ linear combination that breaks the *gerade-ungerade* symmetry. Ultimately this amounts to amend expression [7] by undoing the *g-u* mixing. Consequently, electrons coming from the two *g-u* channels interfere, even and odd electron angular momenta *l* contribute now simultaneously and as a result, the angular distributions become asymmetric with respect to nuclei inversion, mainly when the contributions from the two thresholds overlap at ~ 4 eV and none of them is dominant (see Figure 2 for the correct angular distributions). This fundamental result on symmetry breaking has already been predicted by a time-independent method and confirmed experimentally (6). Nonetheless, the main advantage of the present time-dependent method is the possibility to understand in the time domain the formation and evolution of KED spectra and electron angular distributions. For instance, Figure 4 includes four snapshots at different propagation times during the pulse duration, in which one may appreciate the onset of the autoionization process in the formation of
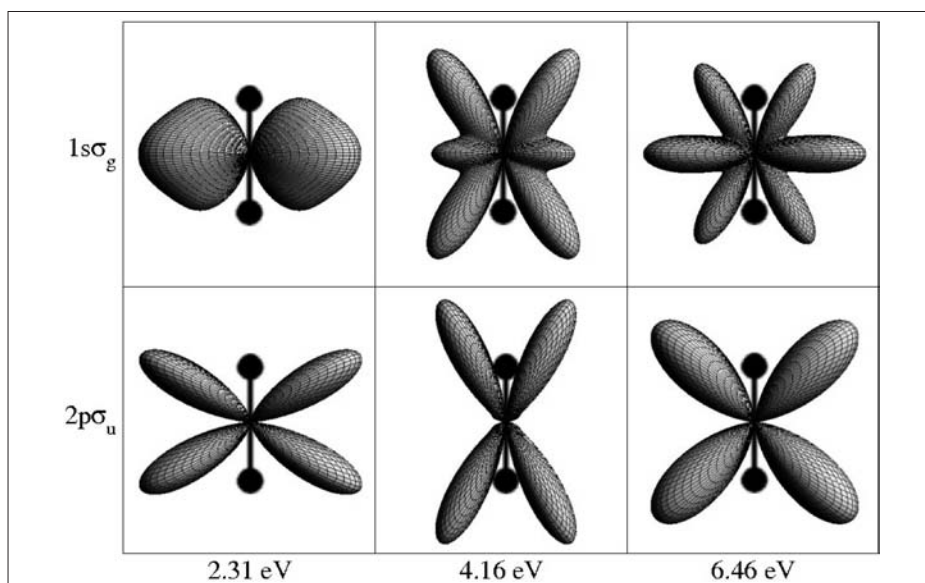
Figure 3. Electron angular distributions (EADs) contributed from the $^2\Sigma_g^+(1s\sigma_g) + e(\pi_u)$ and the $^2\Sigma_u^+(2p\sigma_u) + e(\pi_g)$ ionization channels for the three proton energies quoted in Figure 2. Explanations for EADs in Figure 2 also apply here.
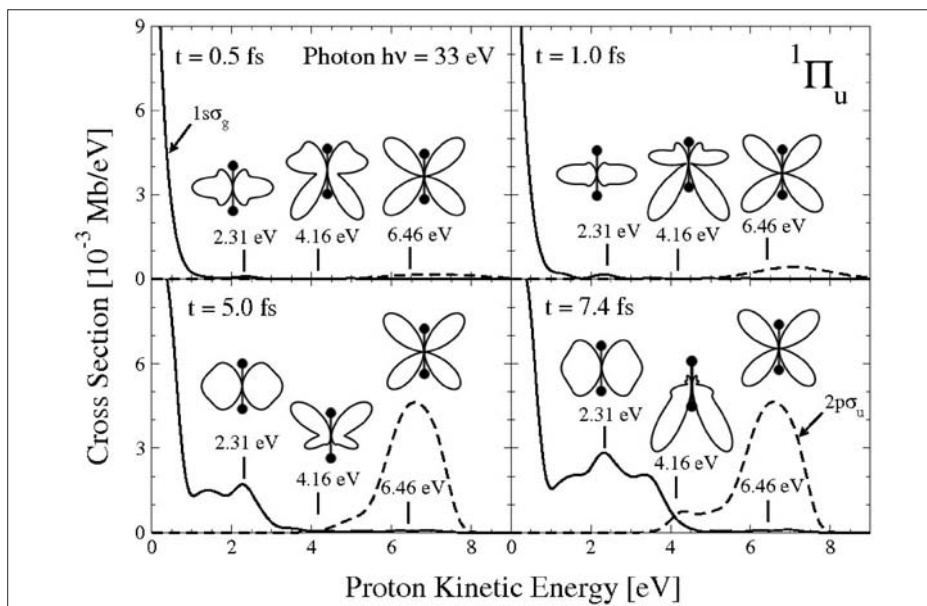

Figure 4. Time evolution for the $^1\Pi_u$ proton kinetic energy distribution (KED) and for the electron angular distributions (EAD) at three proton energies in the dissociative ionization of H_2 mediated by a laser pulse with duration of T = 10 fs and photon energy $\omega = 33$ eV. The propagation time for each snapshot is indicated. Results for t = T = 10 fs are those included in Figure 3.

peaks interference structures in KED and also in the symmetry breaking in the electron angular distributions. Furthermore, this asymmetry seems to be independent to the direction in which the proton is emitted (compare the oscillating nature from t = 5.0 fs and t = 7.4 fs angular distributions at $E_H+ = 4.16$ eV) precluding any explanation of this effect in terms of a post-collisional electron-proton electrostatic interaction.

CONCLUSION

We present a time dependent method to compute proton kinetic energy distributions and electron angular distributions coming from photodissociative ionization of H_2, just the theoretical ingredients to fully compare with kinematically complete experiments (COLTRIMS). Asymmetric photoelectron angular distributions may arise in H_2 (in general, in any symmetric molecule) due to the interference between the *gerade* and *ungerade* electron waves, when the excited molecule decays through autoionization onto two dissociative ionization channels pertaining to different *gerade* or *ungerade* symmetries of the residual molecular ion H_2^+.

ACKNOWLEDGEMENTS

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