

p -H symmetry breaking in dissociative photoionization of H_2 due to the molecular ion interacting with the ejected electron

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We propose a mechanism of electron localization and molecular symmetry breaking in dissociative photoionization of the H_2 molecule. The Coulomb field of the ejected electron can induce the transition of the remaining H_2^+ ion from the gerade $^2\Sigma_g^+(1s\sigma_g)$ to the ungerade $^2\Sigma_u^+(2p\sigma_u)$ electronic state when the nuclei in a bound vibrational state are near the outer turning point. The superposition of this process with a direct transition to the vibrational continuum should produce a nongrade ionic state, which results in observed asymmetry in the p -H ejection relative to the electron ejection direction at a small kinetic energy release.

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Dissociative photoionization (DPI) of the hydrogen molecule has been a subject of considerable interest in recent years. Even though it is a relatively weak single-photoionization channel, the breakup of the H_2^+ ion into the ionic $H^+ \equiv p$ and neutral H atomic fragments allows for determination of the molecular axis orientation when the reaction products are detected in coincidence. Because the dissociation is fast compared with molecular rotation, the direction of fragmentation coincides with the molecular axis at the instant of photoionization. This allows for the molecular frame photoelectron angular distribution to be determined.

One of the striking observations following these coincident studies was breakup of the photoelectron emission symmetry with respect to the ionic p and neutral H atomic fragments. This asymmetry was found in the single-photon-induced DPI process [1–4] as well as in the multiphoton regime [5–10]. The finding of this asymmetry was indeed surprising. The two single-photoionization channels lead from the ground H_2 state to the ionic gerade $^2\Sigma_g^+(1s\sigma_g)$ and ungerade $^2\Sigma_u^+(2p\sigma_u)$ states that are well separated in energy and do not normally mix. Hence, the ionic state possesses a well-defined exchange symmetry which leads to the fully symmetric photoelectron emission. The p -H asymmetry in dissociation means that the asymptotics of the wave function of the state with a fixed ejected electron energy and a fixed nuclear kinetic energy release (KER) is nongrade by the coordinates of the bound electron. From a mathematical point of view, this means that the bound electron is in a superposition of gerade and ungerade H_2^+ wave functions.

Martín *et al.* [2,11] showed that the two ionic states can actually mix because of autoionization via the Q_1 and Q_2 doubly excited states. This creates a mixed-parity ionic state that allows for the localization of the bound electron and angular asymmetry of the photoelectron. Since the autoionizing states live a few femtoseconds, the nuclei have enough time to move outside the Franck-Condon (FC) region before the electron is ejected. Theoretical description of such a process therefore requires going beyond the fixed nuclei Born-Oppenheimer approximation.

An additional mechanism that could be responsible for the photoemission symmetry breaking is the effect of an

intense ir field from few-cycle laser pulses [5,7,10]. The strong laser field may act in conjunction with quantum-mechanical interference involving autoionizing states and the laser-altered wave function of the departing electron. Alternatively, the charge localization may be due to laser-driven transition between different electronic states of the molecular ion.

An alternative mechanism that could be responsible for the DPI asymmetry was discussed briefly by Martín *et al.* [2] in the form of a preferred attractive interaction between the proton and the escaping electron. However, the photoelectron is too fast to be efficiently perturbed by the slow proton, except possibly in the region of the maximum allowed KER. In the present work, we consider a similar mechanism of direct photoelectron interaction with the remaining ion. The Coulomb field of the ejected electron can induce the transition of the remaining H_2^+ ion from the gerade $^2\Sigma_g^+(1s\sigma_g)$ to the ungerade $^2\Sigma_u^+(2p\sigma_u)$ electronic state when the nuclei in a bound vibrational state are near the outer turning point. The superposition of this process with a direct transition to the vibrational continuum should produce asymmetry in the p -H ejection relative to the electron ejection direction at a small kinetic energy release.

The p -H asymmetry in DPI means that the wave function of a state with a fixed ejected electron energy and a fixed nuclear KER is nongrade by coordinates of the bound electron. From a mathematical point of view, this means that the bound electron is in superposition of gerade and ungerade H_2^+ wave functions. The amplitudes of generation of the gerade and ungerade ionic states are proportional to the corresponding FC factor states,

$$S_{gK} = \langle gK | H_2 \rangle, \quad S_{uK} = \langle uK | H_2 \rangle. \quad (1)$$

Here $|H_2\rangle \equiv \chi_{H_2}(R)$ is the ground vibrational state of H_2 , $|gK\rangle \equiv \chi_{KL}^{1s\sigma_g}(R)$ and $|uK\rangle \equiv \chi_{KL}^{2p\sigma_u}(R)$ are vibrational continuum functions of H_2^+ in gerade and ungerade electronic states, respectively, $K = \sqrt{2mE_R}$ is the relative momentum of the ion and atom after dissociation, E_R is the kinetic energy release, m is the reduced mass of a nucleus, and L is the angular momentum transferred to the rest ion in an ionization.

The DPI amplitude via the $2p\sigma_u$ state for $E_R = 1$ eV is less than that via the $1s\sigma_g$ state by ten orders of magnitude

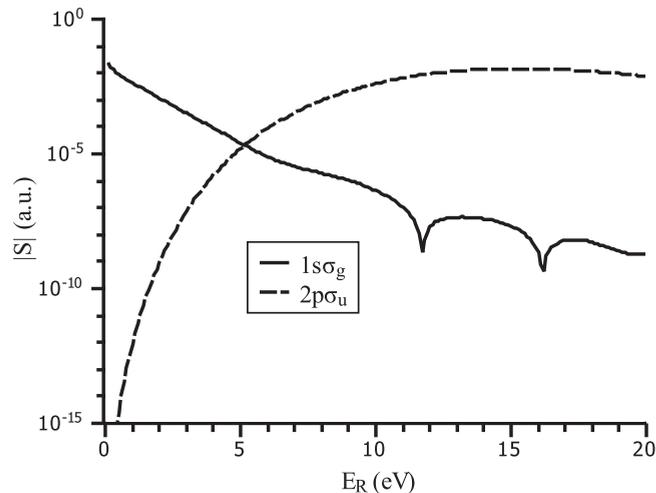


FIG. 1. Absolute values of the overlap integrals between the H_2 vibration ground-state wave function and the H_2^+ vibration continuum for the $1s\sigma_g$ (solid line) and $2p\sigma_u$ (dashed line) electronic states.

(see Fig. 1). Therefore, for small KER, a direct transition to an ungerade state cannot induce an observable asymmetry. It is also clear from a classical physics consideration. The turning point in the $1s\sigma_g$ adiabatic potential for $E_R = 1$ eV is $R = 1.023$ a.u. The turning point in the $2p\sigma_u$ adiabatic potential at the same KER is $R = 4.45$ a.u., well outside the FC region and where the H_2 ground vibration state wave function is extremely small.

The overlap integrals are equal for the gerade and ungerade ionic states at $E_R = 5$ eV. Therefore, the asymmetry of the proton-atom ejection for $E_R = 5$ eV should be similar to the asymmetry of the bound-electron localization immediately after the photoelectron ejection. But the probability of DPI for $E_R = 5$ eV is four orders of magnitude less than for $E_R = 1$ eV. Nearly the same value of KER appears in the case of DPI via a quasistationary state, which can also lead to a strong asymmetry [2,11].

As is clear from the above arguments, DPI with a small KER proceeds solely via the H_2^+ ground state. As a result, the original asymmetry in the bound-electron wave function is lost entirely. To make a transition to a vibrational continuum of $2p\sigma_u$ with a small KER, the ion should reach an internuclear distance close to the turning point in the $2p\sigma_u$ adiabatic potential for a small above-threshold energy. After that, the H_2^+ ion should interact with some external field, which can excite it to the $2p\sigma_u$ state. There are a number of experiments in which an ir laser field with low energy is used for this purpose [5,7,10].

One should note, however, that in the DPI process of H_2 an external field that interacts with the H_2^+ ion is always present. It is the field of the ejected photoelectron. During the time when the internuclear separation reaches sufficient distance to make a transition to a small-KER ungerade state, the ejected electron has already flown far away, and its interaction with the ion is small. However, several effects can conspire to help make the asymmetry from the interaction with far ejected electron observable:

(1) When the ion is in the bound vibrational state with the outer turning point close to inner turning point in the $2p\sigma_u$

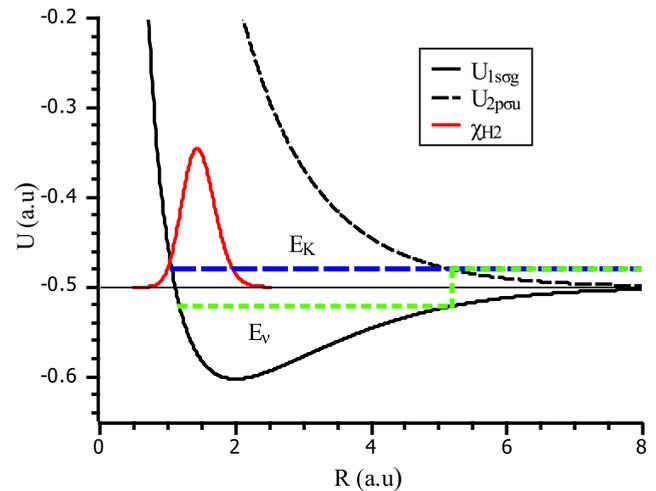


FIG. 2. (Color online) Energy diagram of the proposed DPI process. Shown are the adiabatic potentials for the ionic gerade $1s\sigma_g$ (solid black line) and ungerade $2p\sigma_u$ (dashed black line) states, the initial H_2 vibration state wave function (red solid line), the vibrational continuum energy level and vibrational bound energy level, and the two pathways of dissociation: the direct transition to the continuum energy level E_K (dashed blue line) and via an intermediate vibrational bound state E_V with a following transition of the ion to the $2p\sigma_u$ state (dotted green line).

adiabatic potential (see Fig. 2), the nuclei spend a long time near point R where the overlap between vibrational states is maximal.

(2) The number of ions in bound vibrational states after ionization is much larger than that in vibrational continuum states, and even a small conversion to an ungerade dissociative state can give a result comparable to a direct transfer to a gerade vibrational continuum state.

(3) The $1s\sigma_g$ and $2p\sigma_u$ states form a pair of so-called charge-resonance (CR) states. The energy gap between the CR states decreases with the internuclear distance R , while the dipole transition matrix element $\langle 2p\sigma_u | z | 1s\sigma_g \rangle \rightarrow R/2$. Therefore, CR states are strongly coupled to the external field for large R .

Let us estimate the asymmetry due to this process. We assume that the duration of the ionizing pulse is much smaller than the characteristic time of the nuclear motion. After ejection of the photoelectron, the evolution of the vibrational state can be described by a time-dependent Schrödinger equation,

$$i \frac{\partial \chi_g(R,t)}{\partial t} = \left[-\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{L(L+1)}{2mR^2} + U_{1s\sigma_g}(R) \right] \chi_g(R,t), \quad (2)$$

where $U_{1s\sigma_g}(R)$ is the adiabatic potential. The initial condition imposed on Eq. (2) is that its solution coincides with the H_2 vibrational ground state,

$$\chi_g(R,0) = \chi_{\text{H}_2}(R). \quad (3)$$

The matrix element of the transition between the gerade and ungerade ionic states in the field of the ejected electron is given

by the following expression:

$$\mu(R, r_e) \simeq \frac{d(R)}{r_e^2}. \quad (4)$$

Here r_e is the distance to the ejected electron, and

$$d(R) = \langle 2p\sigma_u | \mathbf{n}_e \cdot \mathbf{r} | 1s\sigma_g \rangle \quad (5)$$

is the dipole matrix element, \mathbf{r} is a coordinate of the bound electron, $\mathbf{n}_e = \mathbf{r}_e/r_e$, $|1s\sigma_g\rangle \equiv \varphi_{1s\sigma_g}(\mathbf{r}; R)$, and $|2p\sigma_u\rangle \equiv \varphi_{2p\sigma_u}(\mathbf{r}; R)$. Equation (4) is derived using the Taylor expansion of $V(\mathbf{r}, \mathbf{r}_e) = 1/|\mathbf{r} - \mathbf{r}_e|$. In the case with $R \gg 1$, the dipole matrix element $d(R) \approx \mathbf{n}_e \cdot \mathbf{R}/2$.

As we expect that the ejected electron is far from the ion at the time of transition, we can describe this electron quasiclassically and assign to it the trajectory $r_e(t)$. Under this assumption, the amplitude of transition to the ungerade state with the asymptotic relative nuclear momentum K can be written as

$$A_{uK} = -i \int_0^\infty \frac{1}{r_e^2(t)} \langle uK | d(R) | \chi_g(R, t) \rangle e^{iE_K t} dt. \quad (6)$$

Here $|uK\rangle \equiv \chi_{KL}^{2p\sigma_u}(R)$ is a solution of the stationary Schrödinger equation,

$$\left[-\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{L(L+1)}{2mR^2} + U_{2p\sigma_u}(R) \right] \chi_{KL}^{2p\sigma_u}(R) = E_K \chi_{KL}^{2p\sigma_u}(R), \quad (7)$$

with $E_K = E_R + U_{2p\sigma_u}(\infty)$. The asymptotic form of the continuum function is $\chi_{KL}^{2p\sigma_u}(R \rightarrow \infty) = \sin(KR + \delta_u)$, where δ_u is a scattering phase. For all the results shown below, the wave functions were obtained by numerical solution of Eqs. (2) and (7).

The results are weakly dependent on the angular momentum L while L is not very large. Typically, L is small when the H_2 molecule is initially in a low rotational state and the angular momentum exchange due to the recoil of the ejected electron is also small. The latter condition is always satisfied when the ejected electron has low energy. For these reasons, the angular momentum $L = 1$ (which corresponds to the ground rotational state of the ortho-hydrogen) was assumed in all examples shown below.

With the simplest approximation $r_e(t) = v_e t$, where $v_e = \sqrt{2E_e}$, with E_e being the ejected electron energy, the equation for the amplitude (6) can be rewritten as

$$A_{uK} = -\frac{i}{E_e} \int_0^\infty a(t) dt, \quad (8)$$

where

$$a(t) = \frac{1}{2t^2} \langle uK | d(R) | \chi_g(R, t) \rangle e^{iE_K t} \quad (9)$$

is the amplitude of transition per unit time.

The modulus of this amplitude is shown in Fig. 3 for selected value of $E_R = 0.4$ eV. Figure 3 supports the qualitative reasoning given above. The noticeable transition begins only when the vibrational wave packet has spread up to the turning point $R(E_R) = 5.49$ a.u. corresponding to $U_{2p\sigma_u}(R) = E_K$. The peak of transition is near $t \approx 700$ a.u. An ejected electron

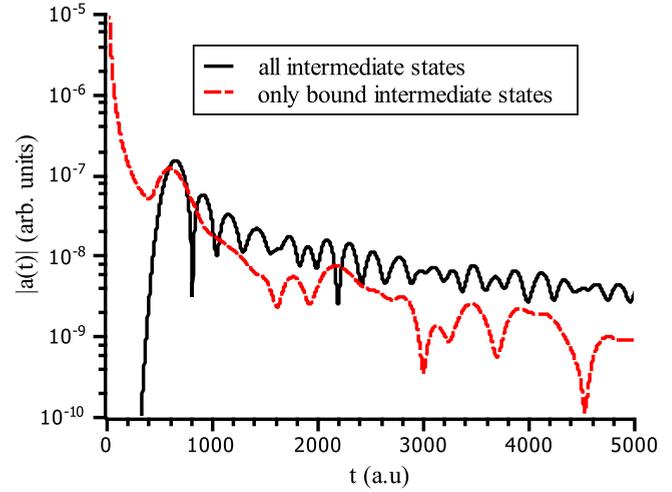


FIG. 3. (Color online) The absolute value $|a(t)|$ of the amplitude of transition per unit time for $E_R = 0.4$ eV from Eq. (9) (solid line) and Eq. (11) (dashed line).

with an energy of, say, $E_e = 2$ eV at this time would reach the distance $r_e \approx 250$ a.u.

It may seem that since the intermediate bound vibrational states make the largest contribution to the process under consideration, we can restrict our account to these states only. In this approximation, the solution of Eq. (2) can be written as

$$\tilde{\chi}_g(R, t) = \sum_v \langle g\nu | \text{H}_2 \rangle \chi_{vL}^{1s\sigma_g}(R) e^{-iE_{vL} t}. \quad (10)$$

The amplitude of transition per unit time (9) takes the form

$$\tilde{a}(t) = \frac{1}{2t^2} \sum_v \langle uK | d(R) | g\nu \rangle \langle g\nu | \text{H}_2 \rangle e^{i\omega_{Kv} t}, \quad (11)$$

where $\omega_{Kv} = E_K - E_{vL}$. However, such an approach is not applicable. In Fig. 3, we compare the moduli of the amplitudes $a(t)$ from Eq. (9) and $\tilde{a}(t)$ from Eq. (11). From this comparison, we see that omitting the continuum from the summation over the intermediate vibronic states causes a serious error. While the position and shape of the main peak do not differ significantly, the amplitude $\tilde{a}(t)$ has an unphysical peak at small t and diverges at $t \rightarrow 0$. This peak appears because omitting the continuum delocalizes the initial wave packet. That is why in calculating A_{uK} we used the direct solution of Eq. (2) instead of the approximated analytical solution given by Eq. (10).

The asymmetry in the p -H ejection can be expressed as [10]

$$\begin{aligned} \beta &= \frac{|S_{gK} e^{i\delta_g} - A_{uK} e^{i\delta_u}|^2 - |S_{gK} e^{i\delta_g} + A_{uK} e^{i\delta_u}|^2}{|S_{gK} e^{i\delta_g} + A_{uK} e^{i\delta_u}|^2 + |S_{gK} e^{i\delta_g} - A_{uK} e^{i\delta_u}|^2} \\ &\simeq -2 \frac{\text{Re}[A_{uK} e^{i(\delta_u - \delta_g)}]}{S_{gK}}, \end{aligned} \quad (12)$$

where δ_g and δ_u are scattering phases for gerade and ungerade states, respectively. Note that according to Eq. (12), the asymmetry parameter $\beta > 0$ corresponds to the case where the bare proton prefers to be ejected in the same direction as the photoelectron, while the H atom is ejected in the opposite direction.

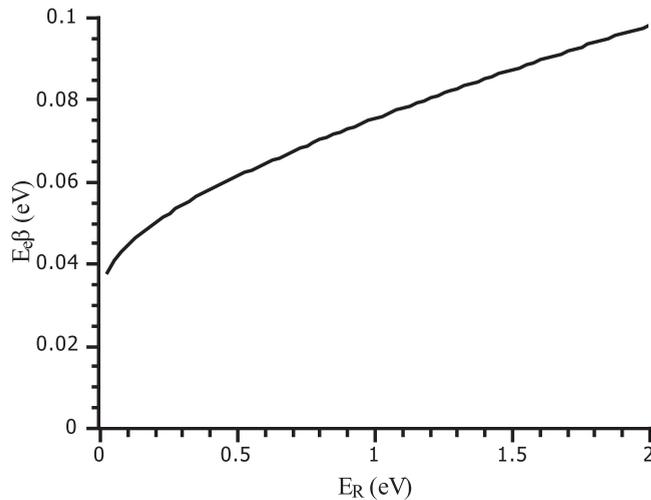


FIG. 4. The scaled asymmetry parameter $\tilde{\beta} = E_e \beta$ as a function of E_R for $\mathbf{R} \parallel \mathbf{n}_e$.

Since the matrix element S_{gK} is real, only the real part of $A_{uK} e^{i(\delta_u - \delta_g)}$ contributes to the asymmetry parameter. The imaginary part of $A_{uK} e^{i(\delta_u - \delta_g)}$ is logarithmically divergent at the upper limit of the integral over t in Eq. (8). This divergence appears in a situation when the ejected electron interacts with the ion born directly in a vibration continuum state. Asymptotically, the internuclear distance in the ion in a vibration continuum state tends to $R(t) \rightarrow v_p t$, where $v_p = K/m$ is the relative velocity of the nuclei. The gerade and ungerade states are degenerate at large R . Following a secular equation, in this case of an ion in an external field, the nondegenerate right and left states are, respectively, $|r\rangle = (|1s\sigma_g\rangle + |2p\sigma_u\rangle)/\sqrt{2}$ and $|l\rangle = (|1s\sigma_g\rangle - |2p\sigma_u\rangle)/\sqrt{2}$. The left and right states describe the two halves of the bound-electron cloud, which is localized near the nuclei. The difference in the potential that the ejected electron affects on these half clouds is $2\mu = 2d(R)/r_e^2 = (\mathbf{n}_R \cdot \mathbf{v}_p/v_e^2)t^{-1}$. As a result, the phase difference of the half clouds is $\sim (\mathbf{n}_R \cdot \mathbf{v}_p/v_e^2) \ln t$. The imaginary part of $A_{uK} e^{i(\delta_u - \delta_g)}$ is proportional to the limit of this phase difference at $t \rightarrow \infty$. However, since the half clouds do not overlap for large R , this phase difference has no effect on any observables.

As follows from Eq. (8), the asymmetry parameter is inversely proportional to the ejected electron energy E_e . So we can introduce the electron-energy-independent asymmetry parameter $\tilde{\beta}(E_R)$ via

$$\beta = \frac{\tilde{\beta}(E_R)}{E_e}. \quad (13)$$

In Fig. 4, the parameter $\tilde{\beta} = E_e \beta$ is shown as a function of KER. To get an unscaled β parameter for a given ejected electron energy E_e , $\tilde{\beta}$ should be divided by E_e in eV. As seen in Fig. 4, for any KER the proton prefers to be ejected in a direction that coincides with the electron ejection direction. When the ejected electron energy is very small and comparable to the excitation energy of the ion, the approximation $r_e(t) = v_e t$ is far too crude because the energy of the ejected electron is changed noticeably after the excitation of the bound electron. Thus, the condition of the validity of Eq. (13) is $E_e \gg E_R$.

In conclusion, we propose a mechanism of p -H symmetry breaking in DPI of H_2 due to the H_2^+ ion interacting with the ejected electron. A seemingly forbidden transition to the ionic $2p\sigma_u$ state at low photon energies is enhanced by final-state interaction with the ionized electron due to the breakdown of the Frank-Condon principle. This mechanism may be responsible for a noticeable asymmetry at low KER. It can be readily observed experimentally using a cold-target recoil-ion momentum spectroscopy (COLTRIMS) coincident detection technique and a synchrotron light source. To resolve the dependence seen in Fig. 4, an energy resolution of the order of 0.1 eV is required. This gives an estimate of the required photon bandwidth, the photoelectron energy, and the KER resolutions. The modern COLTRIMS apparatuses are sensitive to asymmetry down to 5% [10]. To reach such an asymmetry, the energy of the ejected electron should be of the order of 1 eV.

Our estimates are based on the semiclassical approximation of the ejected electron motion. A fully quantum-mechanical treatment is needed to provide a more rigorous estimate for small values of the ejected electron energies. This will require a solution of the fully dimensional time-dependent Schrödinger equation with respect to the electron and nuclear coordinates. This solution was sought and found in Sansone *et al.* [7], but the electronic part of the vibrational states was calculated in a sphere with a radius of 160 a.u. This radius is far too small to account for the effect presently under consideration. However, this approach should reveal the effect after increasing this radius several times.

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