Shifts of Photodetachment Thresholds and Induced Shape Resonances of H^- in an Electric Field

Bin Zhou and C. D. Lin
Department of Physics, Kansas State University, Manhattan, Kansas 66506
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The photodetachment of H^- near the H(N=4) and H(N=5) thresholds in an external electric field is studied theoretically. The recently observed photodetachment threshold shifts by Halka *et al.* are interpreted in terms of the shifts of the barrier heights of the hyperspherical potential curves as the electric field strength is varied. It is shown that higher members of the zero-field Feshbach resonances can emerge as field-induced shape resonances in an electric field.

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Theoretical studies of doubly excited states of atoms and ions over the past few decades have established that the existence and properties of these states owe much to the strong radial and angular correlation between the two excited electrons [1, 2]. The two electrons perform motion akin to the rotation, vibration, and stretching of a floppy triatomic molecule [1, 3–5]. When such an atom is subjected to an external electric field, the radial and angular correlation between the two electrons is brought into competition with the Stark effect of each individual electron. By studying doubly excited states in an external electric field, the nature of correlation between the two excited electrons can be probed.

Over the years, the Stark effect of Rydberg states has been extensively studied, but little has been done for doubly excited states except for the $^1P^o$ doubly excited states of H^- associated with the H(N=2) threshold [6, 7]. It was observed that the Feshbach resonance associated with this threshold is readily quenched in a field of about 100 kV/cm, but the shape resonance is still stable in a field of up to a few MV/cm. A natural question is what would happen if an external field is applied to higher doubly excited states since they extend further away in space from the nucleus and should be more easily affected by the external field. Recently, Halka *et al.* [8] have examined the photodetachment of H^- in electric fields (ranging from 0 to 90 kV/cm) in the energy region where the inner electron is excited to the H(N=4) or H(N=5) states. An example showing the spectra of the production of the H(N=4) cross section for the field strength $F = 0$ and $F = 87$ kV/cm is depicted in Fig. 1 (the vertical scales in the two spectra have been shifted for clarity). Two striking features are apparent by comparing the two spectra: (1) The photodetachment threshold is shifted toward the lower energy side as the electric field is applied. (2) A new window-type resonance (at 13.513 eV) in the H(N=4) cross section emerges when a field of $F = 87$ kV/cm is applied. The experiment measured H(N=4) and H(N=5) cross sections at a number of electric field strengths. It is found that the threshold shift increases with increasing field strength, as shown in Fig. 2. If one takes the viewpoint that the two electrons are independent and that the shifts are due to the linear Stark effect of the inner electron, then the measured threshold shifts are about a factor of 8 (6) too large for N=4 (N=5).

In this Letter we shall give a theoretical interpretation of the above described features observed in the H^- photodetachment in external electric fields. We will show that the apparent shift of excitation thresholds is due to the field effect on both strongly correlated electrons, while the window-type resonances are caused by the coupling between two field-modified channels.

One might start with an intuitive one-channel model by examining the effective potential of the outer electron in an external field. This potential is given by $V(z) = -d/(2z^2) - Fz$ where the first term represents the field of the permanent dipole d of the excited hydrogen atom in the absence of an external field while the second term is

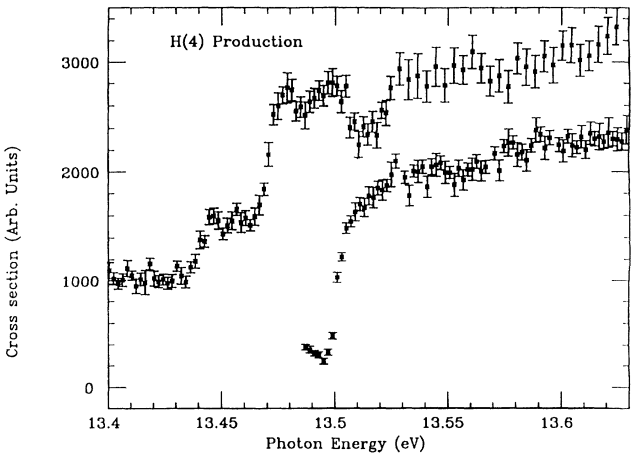

FIG. 1. Relative partial cross section of H(N=4) production vs photon energy near the N=4 threshold for electric field strength $F = 0$ (lower curve) and $F = 87$ kV/cm (upper curve), measured by Halka *et al.* [8]. Note the curve for $F = 87$ kV/cm has been shifted upward by 1000 units for clarity.

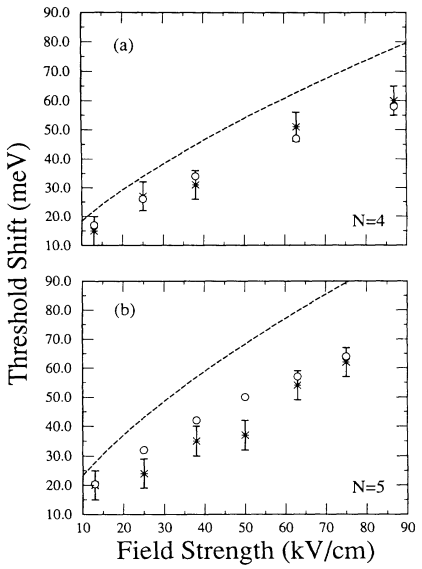

FIG. 2. Absolute values of threshold shifts vs electric field strengths. Experimental results of Halka *et al.* [8] are shown as asterisks and the theoretical predictions from the hyperspherical potential curves are shown as open circles. The dashed lines are obtained using the single-channel estimate: $\Delta E = -\frac{3}{2}d^{1/3}F^{2/3}$. (a) For the N=4 manifold where d=18.46 a.u. (b) For the N=5 manifold where d=37.70 a.u. (see text).

the potential due to an electric field F along the z axis. This potential has a maximum barrier at $z = (d/F)^{1/3}$ where its height is shifted from the zero-field threshold by an amount $\Delta E = -\frac{3}{2}d^{1/3}F^{2/3}$. Since only the $^1P^o(+)$ states are populated in photoabsorption in the zero field [9–11], we take the dipole moment d=18.46 and 37.70 a.u. of the N=4,5 $^1P^o(+)$ channels, respectively. The calculated threshold shifts from this simple model are shown as dashed lines in Fig. 2, which are in reasonable but not perfect agreement with the experimental data [8]. However, this simple one-channel model, which treats the electron correlation as unchanged by the electric field, is not consistent with the quantum mechanical calculation given below. More importantly, it cannot explain the origin of the new window-type resonance observed in the H($N = 4$) cross section in the field $F = 87$ kV/cm.

In the quantum mechanical calculation we solve the Hamiltonian

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} - F\left(z_1 + z_2\right) \tag{1}$$

of an H^- ion in an external electric field F in hyperspherical coordinates. In Eq. (1), r_i is the distance of electron i from the nucleus and z_i is its component along the field direction. In hyperspherical coordinates we replace r_1 and r_2 by the hyperradius $R = \left(r_1^2 + r_2^2\right)^{1/2}$ and the hyperangle $\alpha = \tan^{-1}\left(r_2/r_1\right)$. By treating R as the adiabatic parameter, Eq. (1) is solved at each R to give the hyperspherical potential $U_\mu(R)$,

$$H|_{R=\text{const}}\phi_\mu(R;\Omega) = U_\mu(R)\phi_\mu(R;\Omega), \tag{2}$$

where the index μ denotes the channel, and Ω denotes collectively the hyperangle α and the spherical angles of the two electrons.

In the absence of external fields, the total orbital angular momentum L, spin S, and parity π are good quantum numbers. For a given symmetry L, S, π, channel μ can be identified by a set of approximate quantum numbers K, T, and A which describe radial and angular correlations of the two electrons, and N, which is the hydrogenic principal quantum number of the inner electron [1]. The number of channels for a given symmetry converging to the same threshold becomes large when N is large. For example, for N=4 and 5 there are seven and nine $^1P^o$ channels, respectively, but only the $K > 0$ channels can support Feshbach resonances and only $A = +$ states are dominantly populated in the photodetachment of H^- from its ground state $(K,T)_N^A = (0,0)_1^+\ ^1S^e$ [9,11]. For example, at zero fields the prominent Feshbach resonances below the N=4 threshold [11] belong to $(2,1)^+$. Resonances associated with other channels have not been observed.

In an external electric field, the spherical symmetry of H^- is broken; therefore L and π are no longer good quantum numbers, but S and the projection M of L along the z direction still are. Consequently, one has to include different L,π states in calculating the hyperspherical potentials in an electric field and the size of the matrix will increase drastically. To simplify the calculation and to be able to follow the effect of electric fields on the potential curves, we solve Eq. (2) in two steps. First, eigenstates for F=0 are obtained using the previously developed numerical method [1]. Among the channels that belong to a given symmetry and manifold, only a few of these channels ($K > 0$ channels) are retained as new basis functions to diagonalize the Hamiltonian (2) at different field strengths F. By selecting only the important basis functions from each symmetry, the size of the matrix in the second-step diagonalization is reduced significantly. Specifically, in calculating the potential curves for a given F, we include the lowest two channels for each L for $L < 3$ and the lowest channel for each higher L within the manifold. Basis functions for L up to 14 were included in the calculation.

We first show the potential curves for a few dominant channels that converge to the N=4 threshold in the absence of electric fields [Fig. 3(a)]. For $^1S^e$, $^1D^e$, and $^1G^e$, only the $(3,0)^+$ channels are shown (as dotted lines). For $^1P^o$ (solid lines), and $^1F^o$ (dashed lines), both the $(2,1)^+$ and the $(3,0)^-$ channels are shown [$(2,1)^+\ ^1H^o$, the uppermost dotted line, is also shown]. Note that all the + channels have deeper potential wells at small R, and the − channels have shallow potential wells at larger R. All these potentials approach the same asymptotic limit of $-Z^2/N^2$ in the form of dipole potentials.

In Fig. 3(b), the M=0 potential curves for H^- in an

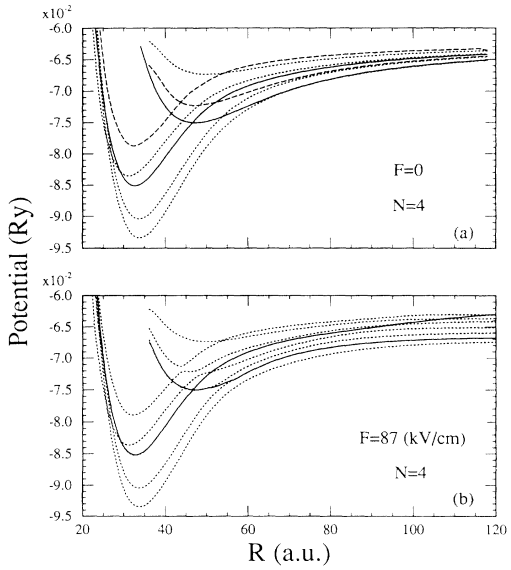

FIG. 3. Hyperspherical potential U_μ of H^- as function of hyperradius R, for $N = 4$ manifold. (a) For $F = 0$: The two solid lines are diabatic $^1P^o(+)$ (lower line) and $^1P^o(-)$ (upper line) potentials; the two dashed lines are diabatic $^1F^o(+)$ (lower line) and $^1F^o(-)$ (upper line) potentials; the dotted lines, from the bottom, are $^1S^e$, $^1D^e$, $^1G^e$, and $^1H^o(+)$ potentials, respectively. (b) For F=87 kV/cm: The dotted curves are adiabatic potentials; the lower (upper) solid line is the diabatic curve which converges to the zero-field $^1P^o(+)$ [$^1P^o(-)$] potential at small R.

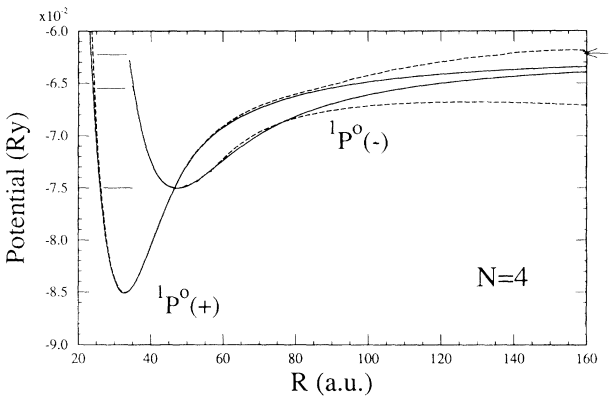

FIG. 4. Comparison between $^1P^o$ diabatic potentials of H^- in F=0 (solid lines) and F=87 kV/cm (dashed lines), for the N=4 manifold. The arrow indicates the position of the zero-field threshold. The energy positions of the three lowest resonance states in the $^1P^o(+)$ potential at F=87 kV/cm are shown by the horizontal bars.

electric field of F=87 kV/cm are shown in the energy region near the H(N=4) threshold. The two curves which correspond to the +/− curves of $^1P^o$ in the F=0 limit are shown as solid curves. These diabatic curves are constructed from the calculated adiabatic curves (dotted lines) using the "noncrossing" rule: Curves that have identical quantum number A are not allowed to cross. This rule does allow an $A = +$ curve to cross any $A = -$ curves. Note that this rule was applied also in constructing the potential curves for each L, S, and π when F=0 [see the +/− curves of $^1P^o$ and $^1F^o$ in Fig. 3(a)].

To demonstrate the effect of electric fields more clearly, in Fig. 4 we isolate the $^1P^o(+,-)$ curves for F=0 (solid lines) and F=87 kV/cm (dashed lines) for the manifold N=4. Since the coupling term in (1) due to the electric field is proportional to R $[(z_1 + z_2) = R(\cos\alpha\cos\theta_1 + \sin\alpha\cos\theta_2)$ where θ_1, θ_2 are the polar angles of the two electrons], effects on the potential curves are expected to be significant only at large R. As one can see, the respective $^1P^o(+)$ and $^1P^o(-)$ curves coincide at small R, while at large R, the $^1P^o(-)$ curve is shifted downward and the $^1P^o(+)$ curve is shifted upward by the electric field. At R=125 a.u., the $^1P^o(+)$ curve rises above the zero-field H(N=4) threshold (at −0.0625 Ry and shown by an arrow in Fig. 4). Eventually this potential will drop at still larger R.

The potential curves shown in Fig. 4 provide the basis for our interpretation of the experimental data of Halka *et al.* [8]. Earlier studies [9–11] have shown that in the zero-field photoabsorption of H^- only states of the $^1P^o(+)$ channel are populated. The potential curve for this channel, as shown in Fig. 4, is shifted *upward* when an electric field is applied. Thus the threshold shifts shown in Fig. 2 cannot be explained by the shift of the $^1P^o(+)$ potential curve alone, as suggested by the one-channel model. However, they can be explained if we consider the coupling between the $^1P^o(+)$ and $^1P^o(-)$ channels.

We first note that the quantum numbers K, T, and A used to classify doubly excited states are not exact. Thus there exist weak residual couplings, most significant near the crossing point, between the +/− channels of Fig. 4. This implies that even if a state is classified by $A = +$, the state always has small $A = -$ components. In the zero-field case, the asymptotic limits of the +/− channels are degenerate, thereby the weak residual coupling has no observational effect directly. When $F \neq 0$, the − curve is pushed downward at large R, resulting in a potential barrier below the zero-field asymptotic limit. Therefore the +/− channel coupling allows the outer electron in the + states populated by photoabsorption to escape or tunnel through the potential barrier of the − channel. As a result, the new threshold of photodetachment in an electric field is determined by the barrier height of the − potential curve, rather than by the shift of the + curve. We note that this mechanism of photodetachment is similar to the predissociation of molecules where a stable bound state belonging to an attractive potential can dissociate when the attractive potential is crossed by a repulsive potential curve.

Based on the above interpretation, we have calculated the shifts of the maximum of the $^1P^o(-)$ potential curve relative to the zero-field threshold for different electric field strengths, and compared the results (shown as cir-

cles) with the experimental threshold shifts of Halka *et al.* for N=4 and N=5 (Fig. 2). In both cases, the agreement with the experimental results is good.

The potential curves in Fig. 4 also serve to interpret the emergence of a new field-induced window-type resonance observed (the dip at 13.51 eV) in the H(N=4) continuum (see Fig. 1) when the field is at 87 kV/cm. This resonance is interpreted as the third lowest resonance associated with the $^1P^o(+)$ potential curve. We have used the WKB approximation to estimate the locations of the lowest three bound states of the $^1P^o(+)$ potential at F=87 kV/cm, and the results are indicated by the horizontal bars in Fig. 4. If we shift the calculated resonance positions by 6 meV such that the lowest resonance coincides with the experimental value 13.338±0.004 eV [11] (the change in the lowest resonance position by the electric field is negligible), the shifted theoretical value for the third resonance is 13.511 eV which is to be compared to the experimental value of 13.513±0.001 eV. In fact, the same calculation shows that the shifted theoretical value for the second resonance position is at 13.467 eV when F=87 kV/cm, which is above the $^1P^o(-)$ potential barrier (see Fig. 4) or the classical photodetachment threshold (about 13.44 eV), and thereby should be seen in the H(N=4) cross section. We suggest that this second resonance manifests itself as the depression in the observed spectra at 13.465 eV (see Fig. 1). (This depression is not small if one contrasts it to a smooth increasing background.) We have used the conversion of 1 Ry =13.5976 eV. It is worthwhile to note that in a strong electric field, due to the coupling between the field-modified $^1P^o(+,-)$ channels, the Feshbach resonances in the N manifold can be seen in the same N continuum spectrum (such as the second and third resonances of N=4 at F=87 kV/cm), instead of being seen in the $N-1$ or lower continuum as in the zero-field photodetachment. Consequently, we call these structures above the H(N=4) threshold in the electric field the "field-induced shape resonances."

In summary, we have calculated the hyperspherical potential curves of H^- for H(N=4,5) manifolds in electric fields. The mixing of different angular momentum states by an electric field changes the electron correlation of high doubly excited H^- states significantly in terms of modified behaviors of diabatic $^1P^o(\pm)$ potentials at large distances. These different behaviors of $^1P^o(\pm)$ potentials, combined with the diabatic coupling between them, are shown to cause the threshold shifts and the field-induced shape resonances observed in the H^- photodetachment in an external electric field.

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