Electric-field-induced modulations in photodetachment

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Recent observations of the effects of a strong electric field on the photodetachment of H^- are accounted for by a frame-transformation analysis. The only input parameter is the binding energy of the negative ion. An absolute cross section that includes the effects of the field is derived. The cross section shows modulations above the detachment threshold. Further, there is now a nonvanishing value below the zero-field threshold as a result of field-assisted tunneling of the photoelectron.

There has been considerable interest in recent years in the effects of long-range external fields, electric and magnetic, on photoabsorption processes in atoms and molecules.[1] A subset of these studies, namely the photodetachment of a negative ion in an electric field,[2] has received less attention than photoionization of neutral atoms in external fields. However, a very recent paper[3] has presented the first detailed experimental data on the photodetachment of a negative ion (H^-) in the vicinity of threshold and in the presence of an electric field ($\simeq 10^5$ V/cm). Having just completed a full theoretical analysis of electric field effects on negative-ion photodetachment,[4] we adapt it to the case of H^- and present our results here. The results for this system are in a particularly transparent form because the zero-field photodetachment near threshold is already well known in a simple form that involves only the binding energy of the negative ion.[5,6] The effects of the electric field enter through a multiplicative modulating factor given analytically in terms of derivatives of Airy functions. Therefore, with no adjustable parameters, we derive an absolute cross section for photodetachment in an electric field, which accounts well for the experimental data. Together with our more detailed presentation,[4] our analysis and equations may be used to describe the photodetachment of any negative ion in an electric field.

We begin with a brief consideration of zero-field photodetachment of H^-. For a weakly bound system such as this, the zero-range approximation[5,6] can be used to describe photoabsorption processes in a particularly simple form. The large scattering length, which exceeds substantially the size of the system, implies that most of the probability distribution is in the exponential tail of the bound-state wave function. A single parameter, the binding energy, suffices therefore to describe adequately the negative ion.[6] The outgoing p electron is also well described by the wave function for a free particle of angular momentum $l=1$, that is,

$$f_{1m}(\mathbf{r})=(2k/\pi)^{1/2}j_1(kr)Y_{1m}(\hat{\mathbf{r}}) \ . \tag{1}$$

This function is normalized per unit energy and we will use atomic units throughout. For a range of energies near threshold, the above function is entirely adequate, the $l=1$ phase shift being very small (even at $k^2=0.01$, the highest energy of interest in this paper, the phase shift is only 0.006 radians[7]). Within this framework, the zero-field photodetachment cross section is easily worked out:[6]

$$\sigma^{F=0}=\frac{16\pi}{3(137)}\frac{\kappa_B}{(\kappa_B^2+k^2)^3}k^3 \ , \tag{2}$$

where $\frac{1}{2}\kappa_B^2=0.7542$ eV is the binding energy of H^-. This result compares[6] very well with experiment and more elaborate theory[8] for a larger energy range even than that which is of interest to us.

The critical energy dependence in (2) is in the k^3 factor (Wigner threshold law[9]). The remaining factor is only weakly dependent on k for $k \ll \kappa_B$. These arise from the long- and short-range parts, respectively, of the electron's motion. The latter's insensitivity to the asymptotic energy is easily understood because at small r there prevail potential energy terms in the e-H system that swamp $\frac{1}{2}k^2$. Viewing (2) as the product of two such factors gives a picture of photoabsorption that is particularly useful for what follows. The first energy-insensitive factor is substantially constant around threshold ($k^2=0$) and can be extrapolated even below threshold. That there is no zero-field photodetachment below threshold can be attributed to the phase-space factor that arises from the large-r part of the wave function which vanishes for $k^2<0$ and rises as k^3 above threshold. As we will see, an external electric field only modifies this long-range part.

The potential due to a static electric field $\mathbf{F}$ in the z direction is Fz. The atomic unit of electric field being 5.14×10^9 V/cm, generally $F \ll 1$. Therefore follows the key conclusion that, for most field strengths of interest, the influence of F is entirely negligible for distances smaller than at least 10^{2-3} a.u. The photoabsorption at small r is, therefore, unaffected by F. Only the long-range propagation of the photoelectron is influenced by the field. The wave function for this range has to be adapted from its zero-field form in (1) to the new cylindrical symmetry that obtains when $F\neq0$. This "frame transformation" is accomplished in two steps, following the pioneering analysis of Fano[10] and Harmin[11] for the similar problem of the photoionization of neutral atoms in an electric field. The final result replaces the previous long-range factor k^3 in (2) by a factor appropriate now to the long-range electric field.

First, still at small distances when the term Fz is small and the electron essentially free, we transform functions from spherical symmetry to cylindrical symmetry. The azimuthal quantum number is common to both schemes and the eigenfunctions of cylindrical symmetry are (J_m is the regular Bessel function)

$$\psi_{qm}(\mathbf{r}) = (2\pi)^{-1/2} e^{im\Phi} J_m((k^2-q^2)^{1/2}\rho)(\pi q)^{-1/2} \times \begin{cases} \cos(qz), & \Pi_z = + \\ \sin(qz), & \Pi_z = - \end{cases} \quad (3)$$

For any energy $\frac{1}{2}k^2$, there are two degenerate solutions of even and odd parity under $z \to -z$. The energy $\frac{1}{2}k^2$ is apportioned into a longitudinal energy $\frac{1}{2}q^2$ for the z motion and an energy $\frac{1}{2}(k^2-q^2)$ for the ρ motion. Expansion of ψ_{qm} in terms of spherical eigenfunctions requires in general all spherical waves f_{lm}, the counterparts of the $l=1$ functions in (1):

$$\psi_{qm}(\mathbf{r}) = \sum_l U_{ql}^{F=0} f_{lm}(\mathbf{r}) \; ; \quad (4)$$

the summation runs over even (odd) $l-m$ for $\Pi_z = +$ $(-)$. Our primary interest is in the $l=1$ coefficient of the transformation matrix $U_{ql}^{F=0}$. Perhaps the simplest procedure to obtain this is to examine both sides of (4) at small values of the distances involved, $\rho, z, r \simeq 0$. This gives

$$U_{q1}^{F=0} = \begin{cases} (3q/k^3)^{1/2}, & m=0 \quad (5a) \\ (3/2kq)^{1/2}(1-q^2/k^2)^{1/2}, & m=\pm 1 \; . \quad (5b) \end{cases}$$

The second step of the frame transformation is to match the energy normalized wave function of the photoelectron in the field Fz, namely, (Ai is the regular Airy function[12])

$$\psi_{qm}^F = (2\pi)^{-1/2} e^{im\Phi} J_m((k^2-q^2)^{1/2}\rho)(4/F)^{1/6} \times \mathrm{Ai}[(2F)^{1/3}(z-q^2/2F)] \; , \quad (6)$$

to the $F=0$ functions in (3) at small z. We have

$$\psi_{qm}^F = A\psi_{qm}(\Pi_z=+) + B\psi_{qm}(\Pi_z=-) \; . \quad (7)$$

Upon evaluating both sides at $z=0$, we obtain

$$A = (\pi q)^{1/2}(4/F)^{1/6}\mathrm{Ai}[-q^2/(2F)^{2/3}] \; , \quad (8a)$$

$$B = (\pi/q)^{1/2} 2^{2/3} F^{1/6}\mathrm{Ai}'[-q^2/(2F)^{2/3}] \; . \quad (8b)$$

The full frame transformation between the functions in (6) and (1), obtained upon combining the two steps, gives

$$\psi_{qm}^F = \sum_l U^F{}_{ql} f_{lm} \; , \quad (9)$$

with

$$U_{q1}^F = \begin{cases} (3\pi/k^3)^{1/2}(16F)^{1/6}\mathrm{Ai}'[-q^2/(2F)^{2/3}], & m=0 \quad (10a) \\ (3\pi/2k)^{1/2}(4/F)^{1/6}(1-q^2/k^2) \times \mathrm{Ai}[-q^2/(2F)^{2/3}], & m=\pm 1 \; . \quad (10b) \end{cases}$$

Since, according to our earlier remark about a negligible $l=1$ phase shift, we do not need the corresponding transformations for irregular functions, we defer that discussion as well as the more general analysis for photodetachment in an electric field to our longer paper.[4] Here it suffices to note that for the cross section in the presence of the field we have to use (6) for the final-state wave function and, therefore, given (9), we have

$$\sigma^F(k) = \sigma^{F=0}(k) \int_{-\infty}^{k^2/2} d(q^2/2)\, |U_{q1}^F|^2 \equiv \sigma^{F=0} H^F(k) \; . \quad (11)$$

The cross section for $F=0$ is modified by a multiplicative factor $H^F(k)$, called the "modulating factor."[4,11] Note that it involves an integration of $|U_{q1}^F|^2$ over all possible values of the longitudinal energy $\frac{1}{2}q^2$ for a given total energy $\frac{1}{2}k^2$. For $F \neq 0$, since the potential Fz falls to $-\infty$ at $z=-\infty$, this sets the lower limit of the integral; the upper limit is set by the requirement of positive transverse energy, $\frac{1}{2}(k^2-q^2) \geq 0$.

Figure 1 compares the recent experimental data[3] on photodetachment of H^- with the result in (11) upon combining it with (2). The following three features are worthy of note.

(a) Above the zero-field detachment threshold, σ^F oscillates about the $\sigma^{F=0}$ value. These oscillations decrease in wavelength with increasing photon energy. The amplitude of the oscillations is proportional to $F^{1/3}$. We show the results for $m=0$. Oscillations are also present for the other polarization, $m=\pm 1$, but of much weaker amplitude and larger wavelength as a result of the second factor in (5b).

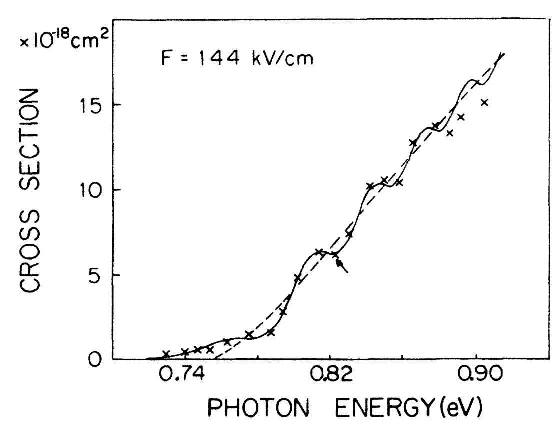

FIG. 1. Photodetachment cross section of H^- with [——, Eq. (11)] and without [— — —, Eq. (2)] an electric field, compared with experimental data (×) for π polarization. The experimental results are normalized to the theoretical ones at the point marked by the arrow.

(b) σ^F is finite at $k=0$ with a value that is proportional to F.

(c) σ^F is nonzero below the zero-field detachment threshold and decreases rapidly and monotonically from its value at threshold.

All these features can be understood on the basis of the analytical structure of $H^F(k)$ and in terms of the simple physical picture that has guided our analysis. For $k^2>0$, the integral in (11) that defines $H^F(k)$ can be split into two ranges, $(-\infty,0)$ and $(0,\frac{1}{2}k^2)$. The former, which equals $H^F(0)$, may be evaluated analytically[4,13] and gives

$$H^F(0)=\Gamma(\tfrac{1}{3})\Gamma(\tfrac{2}{3})(F/\pi k^3) . \tag{12}$$

The integral from 0 to $\frac{1}{2}k^2$, on the other hand, oscillates with increasing k as more loops of the Airy function or its derivative are embraced by the integrand. This accounts for (a) and (b) above. Note, in particular, the $1/k^3$ in (12) which cancels precisely the sensitive energy-dependent factor in (2) in the zero-field cross section. This is as expected because the factor k^3 in (2), stemming from the long-range field in that situation (the angular momentum barrier) is replaced now by the factor appropriate to Fz.[14] The point (c) above is also understood in terms of $H^F(k)$ being continuous at $k\simeq 0$ unlike the zero-field long-range factor which vanishes for $k^2<0$ and increases as k^3 for $k^2\geq 0$. In fact, for $k^2<0$, we have[15] (with $k^2=-\kappa^2$)

$$H^F(\kappa)=\int_{-\infty}^{-\kappa^2/2} d(q^2/2)\,|\,U_{q1}^F\,|^2$$

$$\simeq(3F/4\kappa^3)\exp(-2\kappa^3/3F),\quad \kappa\gg 1 . \tag{13}$$

The above results may conveniently be viewed (Fig. 2) in terms of our analysis which splits photodetachment into two parts. The first, the absorption of the photon at small r, lifts the electron within the e-H potential well to the energy position marked c or d, depending on whether $\frac{1}{2}k^2$ is <0 or >0. This part is entirely insensitive to the presence or absence of the electric field potential (the long diagonal line in Fig. 2) and also to small differences in $\frac{1}{2}k^2$. In zero-field photodetachment, when the diagonal line in the figure is absent, the second part of the process, namely, the outward propagation of the photoelectron from $r\simeq 0$ to infinity is not possible for c whereas it can occur for d. The probability of reaching infinity is thus nonzero only above threshold and is sensitive to how far above threshold the energy lies. Note that the electron has to tunnel out through the angular momentum barrier.[16] In the presence of an electric field, the second part of the process is modified as follows. Now the photoelectron can escape to $z=-\infty$ at all energies, that is, both for c and d. For the latter, this long-range evolution is still through the p-wave barrier but now also against the backdrop of a linearly falling potential which impresses modulations on the photoelectron wave function, and, therefore, on the cross section. For a point such as c that lies below the zero-field detachment threshold, the photoelectron can also escape from $z\simeq 0$ to $z=-\infty$, but this requires a tunneling through the electric field's potential barrier. Not surprisingly, the lower point c is below the threshold, the larger the barrier and the smaller (exponentially) the probability of tunneling out to $z=-\infty$. The formulas above, (12) and (13) in particular, and the results in Fig. 1 reflect these features of the photodetachment process at and in the vicinity of the zero-field detachment threshold.

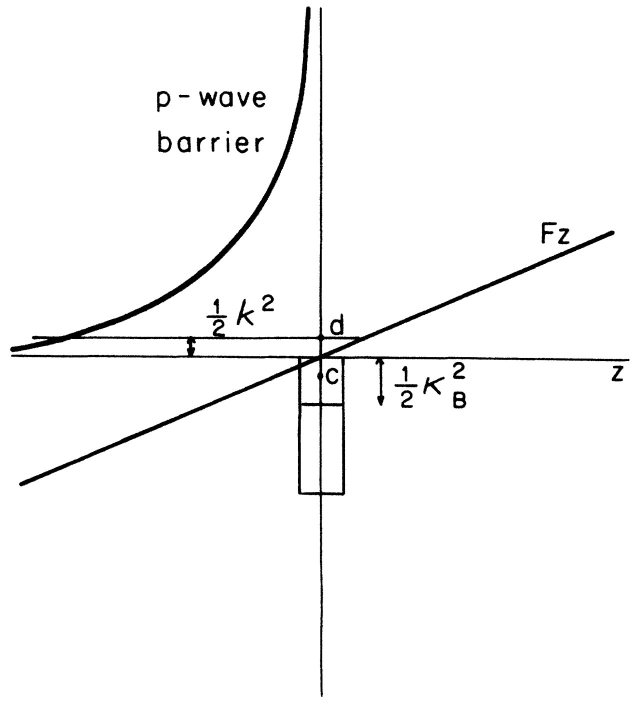

FIG. 2. Schematic of photodetachment. For $F=0$, reading only the left half of the diagram, with the abcissa regarded as the radial coordinate, absorption of the photon within the short-range potential reaches c (below threshold) or d (above threshold). Escape is only possible for the latter, and the electron has to tunnel outward through the angular momentum barrier. For $F\neq 0$, the entire diagram is involved, the abcissa now the z coordinate. Escape to $z=-\infty$ is now possible for both c and d, and involves penetration of the combined potential represented by the p-wave barrier and the downward sloping straight line Fz.

Finally, it is worthwhile to connect these modulations seen in photodetachment to the above-threshold resonances in the photoionization of neutral atoms through a model[17] that embraces all such phenomena. These phenomena in an electric field, when viewed in parabolic coordinates, involve motion simultaneously in two coordinates, $\xi=r+z$ and $\eta=r-z$. The former motion has always a discrete spectrum, the positions and separations of the energy levels marking the positions of the resonances or modulations. For photoionization near threshold, these positions are *equally spaced*[17] with a spacing that is proportional to $F^{3/4}$. On the other hand, for photodetachment, the potential for the ξ motion reduces to a triangular well. The well-known expression for the energy levels in such a potential,

$$E_n = \frac{(3\pi)^{2/3}}{2}(Fn)^{2/3} , \quad (14)$$

marks the positions of the maxima in the modulations above threshold, in good agreement with the experimental data.

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[14]For $F=0$, the width of the barrier is determined by $1/r^2=\frac{1}{2}k^2$ and, therefore, given by $\sqrt{2}/k$. On the other hand, for $k\simeq 0$ when $F\neq 0$, the width is given by $(1/z^2)+Fz=0$ and equals $F^{-1/3}$, independent of k. In both cases, the cross section depends on the inverse third power of the barrier width (see Ref. 16).

[15]Ref. 12, Sec. 10.4.61.

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