The influence of electric field on the photodetachment of H^- near a metal surface*

Huang Kai-Yun(黄凯云) and Wang De-Hua(王德华)†

School of Physics, Ludong University, Yantai 264025, *China*

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The influence of electric field on the photodetachment of H^- near a metal surface is investigated based on the closed-orbit theory. It is found that the photodetachment of H^- near a metal surface is not only related to the electric field strength but also to the electric field direction. If the electric field is along the $+z$ axis, it can strengthen the oscillation in the photodetachment cross section. However, if the electric field is along the $-z$ axis, since the direction of electric field force is opposite to that of static-image force caused by the metal surface, the situation becomes much more complicated. When the electric field is very weak, its influence can be neglected. The photodetachment cross section is nearly the same as that when a single metal surface exists. When the electric field strength is strong enough, the electric field force is able to counteract the metallic attraction, therefore no closed orbit is formed. If the electric field continues to increase until its influence becomes dominant, the photodetachment cross section approaches the case of the photodetachment of H^- in an electric field. Our results may be useful for guiding future experimental studies on the photodetachment of negative ions near surfaces.

Keywords: closed-orbit theory, photodetachment, electric field, metal surface

PACC: 3450D, 3280F, 0365S

1. Introduction

A lot of studies have shown that atoms or ions in external fields or near surfaces show quite different properties from those in free space.[1−10] Interest in the photodetachment of negative ions in external fields can be traced back to the work of Blumberg in early 1979. They found that the photodetachment cross section of a negative ion in a magnetic field was shown to have an oscillatory structure depending on the photon energy.[1] In 1987, Bryant *et al.* observed a ripple-like structure in the photodetachment cross section of H^- in the presence of electric fields.[2] Later on, Rau and Wong explained the "ripple" structure as an interference between the detached electron waves going up and down the electric potential hill.[3] Subsequently, Du and Delos have developed a closed-orbit theory to interpret the "ripple" structure. They pointed out that the oscillations in the cross section were caused by the closed orbits of the detached electron.[4] Recently, much attention has been paid to the photo-induced electronic excitations of adsorbates on metal surfaces.[5] Since H^- has been proposed to be used to probe adsorbate state lifetime and charge transfer during backscattering,[6] the photodetachment of H^- near an interface has attracted much interest. In 2006, Yang *et al.* applied closed-orbit theory to study the photodetachment of H^- near an elastic interface.[7] Later on, many authors studied the photodetachment of H^- near an elastic interface in different external fields.[8−10] In these early studies, they all considered the interface as an elastic wall, and the interaction potential between the electron and the surface is neglected and the collision of the electron with the surface is elastic. Therefore, this system is a real integrable one and the classical motion of the detached electron is analytical, and its theoretical treatment is relatively easy. However, the elastic wall is only a simple model, which is different from a real surface. For the photodetachment of a negative ion near a metal surface, the detached electron will be subjected to the fields caused by the presence of image charge in the metal surface, thus this system becomes a nonintegrable one. Its theoretical analysis is complicated. Recently, Zhao *et al.* investigated the photodetachment of H^- near a metal surface.[11,12] In their work, the photodetachment cross section has changed a little only in a small energy region above the

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†Corresponding author. E-mail: jnwdh@sohu.com

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threshold. Then how to control the photodetachment of H^- near a metal surface is an interesting research subject. Since the influence of the metal surface on the detached electron is similar to the case of the electric field, we can use the electric field to control the photodetachment of H^- near a metal surface. In our previous study, we investigated the photodetachment of H^- in a uniform electric field near a metal surface.[13] In that case, we kept the electric field constant and studied the variation of the photodetachment cross section with the change of ion-surface distance. As to the influence of a varying electric field on the photodetachemnt of H^- near a metal surface, no discussions have been given. In the present work, we keep the ion-surface distance at a given value and discuss in particular the influence of the electric field on the photodetachment of H^- near a metal surface. The results show that the photodetachment cross section is not only related to the electric field strength but also related to the direction of the electric field.

This paper is organized as follows. In Section 2, we describe the Hamiltonian for the system of H^- in an electric field near a metal surface. In Section 3 we first describe the classical motion of the detached electron in different electric fields near a metal surface and find out the closed orbits of this system. Then we derive an analytical formula for the photodetachment cross section of H^- in an electric field near a metal surface by using the closed-orbit theory. Some calculation results and discussions are given in Section 4. Section 5 gives some conclusions of this paper. Atomic units are used throughout this work unless indicated otherwise.

2. Hamiltonian

A schematic diagram is shown in Fig. 1 for the detached electron and its interaction with the metal surface and the electric field. Take the direction of the electric field as the z-axis and use the cylindrical coordinates (ρ, z, ϕ). A hydrogen negative ion H^- sits at the origin and a z-polarized laser is applied for the photodetachment. A metal surface perpendicular to the z-axis is put at $z = -d$, where d is the ion-surface distance. As in the previous studies,[8] H^- can be regarded as a one-electron system, with the active electron loosely bound by a short-range potential $V_{\rm b}(r)$ of the hydrogen atom, where r is the position of the detached electron relative to the hydrogen atom.

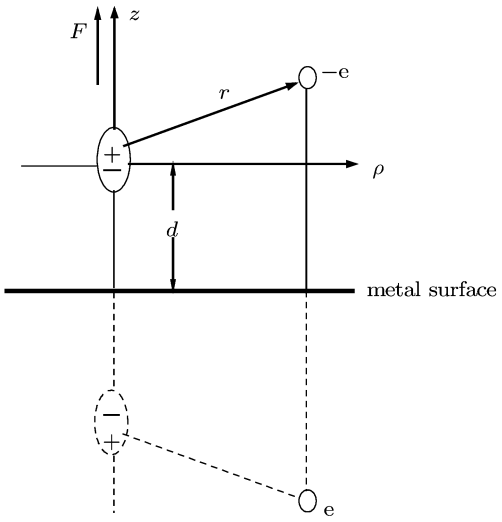


Fig. 1. Schematic representation of H^- in an electric field near a metal surface, with the electric field along the $+z$ axis.

When H^- absorbs a photon, the active electron is detached and moves away from the hydrogen atom. According to the electrostatic image method,[14] the potential acting on the active electron in the ion-surface system includes three parts: $V = V_{\rm b} + V_{\rm c} + V_i$, in which $V_{\rm c}$ is the interaction of the active electron with the image hydrogen atom, which is also a short-range potential. $V_{\rm i}$ is the interaction potential between the active electron and the image electron: $V_{\rm i} = -1/4(d+z)$. The interaction between the active electron and the hydrogen atom and the image of the hydrogen atom can be neglected after the electron is detached. Therefore the Hamiltonian governing the motion of the detached electron can be described as

$$H = \frac{1}{2}\left(P_\rho^2 + \frac{L_z^2}{\rho^2}\right) + \frac{1}{2}P_z^2 - \frac{1}{4(d+z)} + \frac{1}{4d} \pm Fz, \quad (1)$$

where the plus sign corresponds to the upward electric field and the minus sign corresponds to the downward one; $1/4d$ is a constant which is added to shift the potential such that the value of the potential at the origin is zero. Due to the cylindrical symmetry of the system, the canonical angular momentum L_z is a constant of motion. For simplicity, we take it as zero.

3. Closed-orbit theory for the photodetachment cross section

Closed-orbit theory gives the following physical picture for the photodetachment of H^- in an electric field near a metal surface. When H^- absorbs photon energy $E_{\rm ph}$, outgoing electron waves are generated.

These outgoing waves can propagate large distances. Due to the effect of the electric field and the metal surface, however, they cannot propagate to infinity, some of the waves are turned back by the electric field and the surface and return to the origin. Finally, the returning waves overlap with the outgoing source waves to give the oscillating structure in the photodetachment cross section. In all the classical trajectories of the photodetached electron emanating out from the origin, only those bounced back by the electric field and the metal surface to the origin are called closed orbits. Closed-orbit theory gives a prescription for calculating the oscillations in the photodetachment cross section from the closed orbits, once we have all the closed orbits of the detached electron of the system.

3.1. Closed orbits

We now search for all the closed orbits. Consider the following two special cases.

(i) The electric field is along the $+z$ axis

The Hamiltonian for this system can be described by Eq. (1). By solving the Hamiltonian equation of motion, we find that the motion in the ρ direction is free,

$$\rho(t) = R\sin\theta + kt\sin\theta, \tag{2}$$

where R is the initial spherical radius, θ is the outgoing angle of the detached electron and $k = \sqrt{2E}$ is the momentum.

Due to the free motion in the ρ direction, the only closed orbit is along the $+z$ axis. This orbit leaves the origin and moves along the positive direction of the z axis. Then it is slowed down, stopped and attracted back to the origin by the influence of electric field and the metal surface. Some of the detached electron's trajectories are shown in Fig. 2(a); the closed orbit is marked by the darker line. This case is like the photodetachment of H^- near a metal surface.[11]

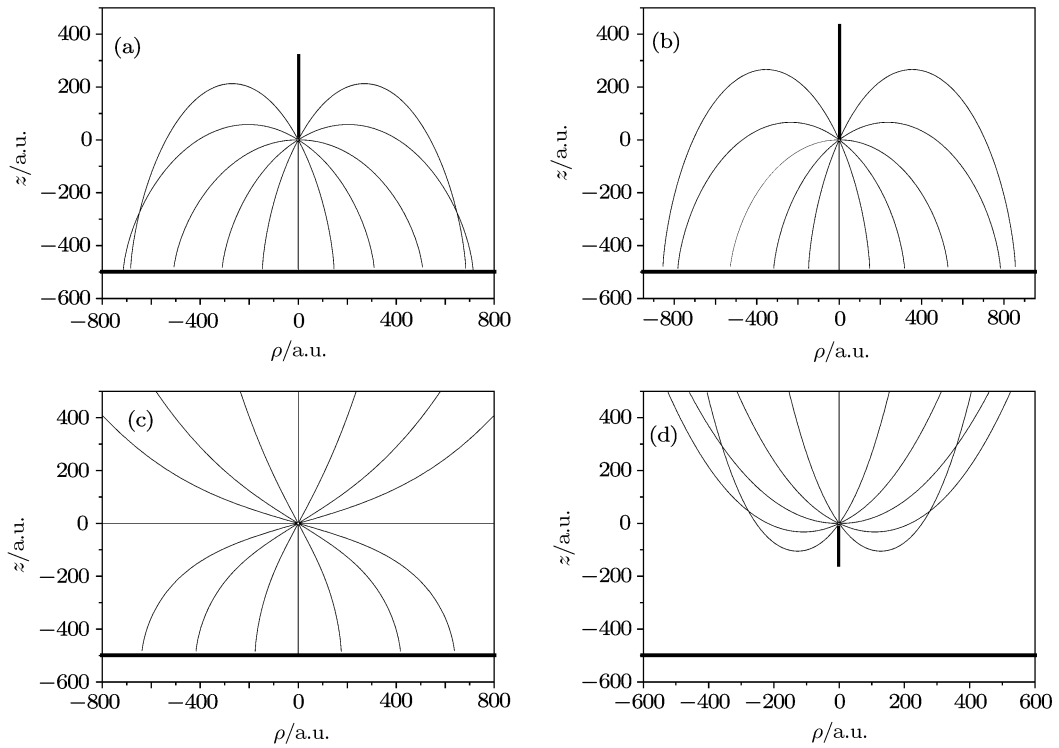


Fig. 2. Some trajectories of the detached electron in an electric field near a metal surface. The distance between the ion and metal surface is $d = 500$ a.u (atomic units). The closed orbit is marked by the vertical darker line in each plot. (a) The electric field is along the $+z$ axis with the strength $F = 500$ V/cm, only one upward closed orbit exists. (b) The electric field is along the $-z$ axis, the electric field strength is relatively small, $F = 80$ V/cm, only one upward closed orbit exists. (c) The electric field is along the $-z$ axis, with the electric field strength $F = 5.14$ kV/cm, no closed orbit exists. (d) The electric field is along the $-z$ axis, with the electric field strength $F = 15$ kV/cm; only one downward closed orbit exists.

(ii) The electric field is along the $-z$ axis

By solving the Hamiltonian equation of motion, we find the motion in the ρ direction is still free. The closed orbit is still along the z axis. However, for the downward electric field, the electric field force acting on the detached electron is in the opposite direction to the metallic attraction force, so the situation becomes much more complicated. The calculation results suggest that if the electric field is relatively weak, its force cannot counteract the metallic attraction, then only one closed orbit along the $+z$ axis exists (see Fig. 2(b)). Increase the electric field strength until its influence is able to counteract the metallic attraction. Under this situation, no closed orbit exists, as we can see from Fig. 2(c). If we continue to increase the electric field, then a closed orbit appears again. But it is along the $-z$ axis in this case (see Fig. 2(d)).

3.2. Photodetachment cross section

According to the closed-orbit theory the photodetachment cross section of H^- in an electric field near a metal surface can be divided into two parts,

$$\sigma(E,F,d) = \sigma_0(E) + \sigma^{\rm osc}(E,F,d). \tag{3}$$

The first part is the photodetachment cross section of H^- without any external fields or metal surfaces:[8]

$$\sigma_0(E) = \frac{16\sqrt{2}B^2\pi^2E^{3/2}}{3c(E_{\rm b}+E)^3},$$

where $B = 0.31522$ is a normalisation function constant, c is the speed of light and its value is approximately 137 a.u., $E_{\rm b}$ is the binding energy of H^- and it is approximately equal to 0.754 eV.

The second part is the oscillating term, which corresponds to the contribution of the returning wave travelling along the closed orbit[4]

$$\sigma^{\rm osc}(E,F,d) = -\frac{4\pi}{c}(E+E_{\rm b}){\rm Im}\left\langle D\psi_{\rm ini}|\psi_{\rm ret}\right\rangle, \tag{4}$$

in which $\psi_{\rm ini}$ is the initial bound state wave function of H^- and is given by $\psi_{\rm ini} = B{\rm e}^{-k_{\rm b}r}/r$, with $k_{\rm b} = \sqrt{2E_{\rm b}}$, and D is the dipole operator. For z-polarized light, we have $D = z$; $\psi_{\rm ret}$ is the returning part of the detached electron wave, which represents the electron wave propagating outward into the external region first, then being bounced back by the electric field and the metal surface, and finally returning to the vicinity of the ion core along the closed orbit. In order to obtain the returning wave function associated with each closed orbit, we draw a sphere of radius $R \approx 5.0$ a.u. The outgoing wave on the surface of this sphere is then[11] given by

$$\psi^0(R,\theta,\phi) = -{\rm i}\,\frac{4Bk^2}{(k_{\rm b}^2+k^2)^2}\cos(\theta)\frac{{\rm e}^{{\rm i}(kR-\pi)}}{kR}. \tag{5}$$

When this wave propagates out from the ion core and travels along the closed orbit, its phase and amplitude changes. In the semiclassical approximation, the wave outside this sphere is a sum of the above outgoing waves

$$\psi_(r) = \sum_j \psi^0(R,\theta,\phi)A_j{\rm e}^{{\rm i}(S_j-\mu_i\pi/2)}, \tag{6}$$

where the sum runs over all the electron closed orbits, S_j and μ_j are respectively the action and Maslov index of the closed orbit j. A_j is the amplitude of the closed orbit, which is given by

$$A_j(\rho,z,\phi) = \left|\frac{J_j(\rho,z,0)}{J_j(\rho,z,T)}\right|^{1/2};$$

$J_j(\rho,z,T)$ is the Jacobian

$$J(\rho,z,\phi) = \rho(T)\left|\begin{array}{cc}\dfrac{\partial z}{\partial t} & \dfrac{\partial z}{\partial\theta}\\ \dfrac{\partial\rho}{\partial t} & \dfrac{\partial\rho}{\partial\theta}\end{array}\right|. \tag{7}$$

Due to the classical motion of the detached electron, the amplitude is given by

$$A_j(\rho,z,\phi) = \left|\frac{P_{z0}}{P_{zt_j}}\right|^{1/2}\frac{R}{R+kt_j}. \tag{8}$$

Equation (8) is valid for the propagation from the sphere of radius R out and back to the same sphere. Inside the sphere, the wave function can be approximated by an incoming plane wave. When the returning wave comes back close to the nucleus, it can be approximated by a plane wave travelling in the z-direction

$$(\psi)^j_{\rm ret}(r\approx 0) = N_j{\rm e}^{{\rm i}\,k_z^{\rm ret}z}, \tag{9}$$

where N_j is a matching factor. According to the general method given by Du and Delos,[4] we have

$$N_j = \tilde{A}_j{\rm e}^{j(S_j-\pi/2)}\psi^0(R,\theta,\phi), \tag{10}$$

in which,

$$\tilde{A}_j = \frac{1}{kT_j}. \tag{11}$$

Here T_j is the period of the closed orbit. From the analysis in Subsection 3.1, we know there is only one closed orbit whether the electric field is upward

or downward, therefore we denote the period of the closed orbit by T in the following part.

Substituting the above equations into Eq. (4) and carrying out the overlap integral, we obtain the oscillatory part of the photodetachment cross section

$$\sigma^{\rm osc}(E,F,d)=\frac{8\pi^2B^2\sqrt{2E}}{c(E_{\rm b}+E)^3T}\cos(S), \qquad (12)$$

in which T and S are the period and action of the closed orbit. By solving Eq. (1), the momentum of the outgoing detached electron along the closed orbit can be written as

$$P_z=\pm\sqrt{2\left(E-\frac{1}{4d}-Fz+\frac{1}{4(d+z)}\right)}, \qquad (13)$$

where the plus sign corresponds to upward closed orbits and the minus sign to downward ones. When the detached electron reaches the top ($z=z_{\rm top}$) of the closed orbit, its z-momentum $P_z=0$. Setting P_z to zero, we can obtain the turning point of the closed orbit $z_{\rm top}$ in the two cases. The period of each closed orbit is given by

$$T=2\int_0^{z_{\rm top}}\frac{1}{P_z}{\rm d}z. \qquad (14)$$

The action of the closed orbit is given by

$$S=2\int_0^{z_{\rm top}}P_z{\rm d}z. \qquad (15)$$

Finally, substituting T, S into Eq. (12), we obtain the value of $\sigma^{\rm osc}(E,F,d)$. Therefore, the total photodetachment cross section of H^- in an electric field near a metal surface is given by

$$\sigma(E,F,d)=\frac{16\pi^2\sqrt{2}B^2E^{3/2}}{3c(E_{\rm b}+E)^3}+\frac{8\pi^2B^2\sqrt{2E}}{c(E_{\rm b}+E)^3T}\cos(S). \qquad (16)$$

Equation (16) is valid whether the direction of the electric field is upward or downward.

4. Results and discussion

Using Eq. (16), we calculated the photodetachment cross section of H^- in different electric fields near a metal surface. In all of our calculations, we keep the ion-surface distance unchanged ($d=500$ a.u.).

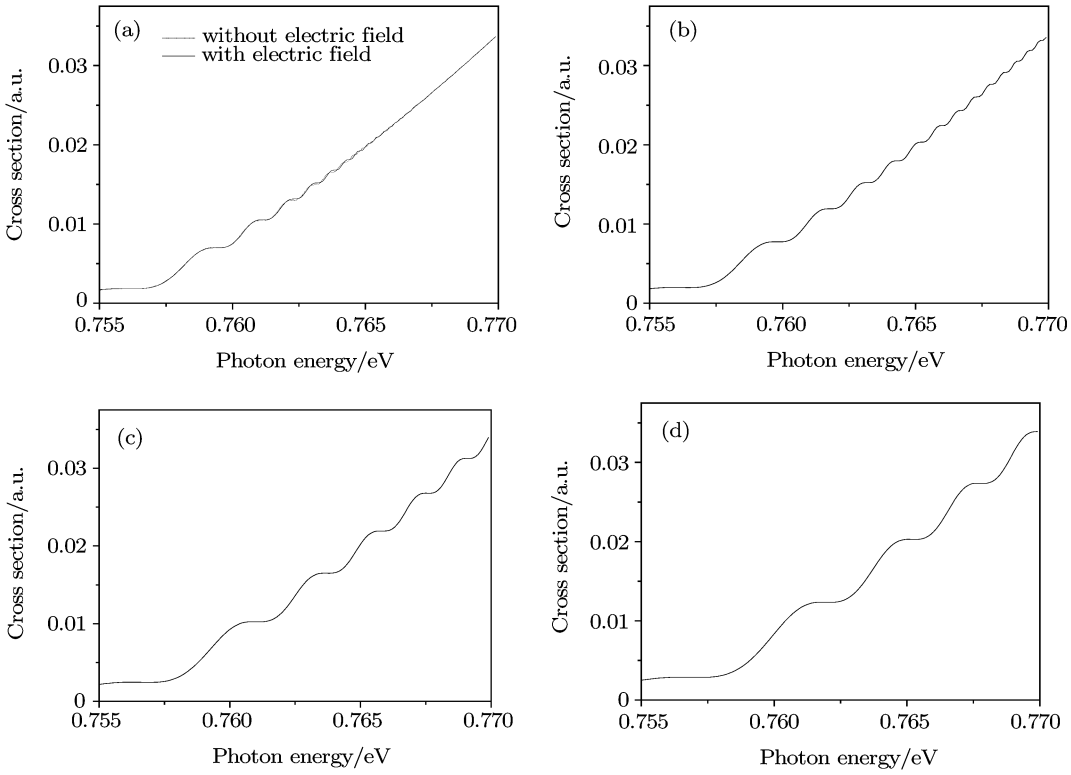


Fig. 3. Photodetachment cross section of H^- in an upward electric field near a metal surface. The distance between the ion and metal surface is $d=500$ a.u. (a) $F=25$ V/cm, the solid line is the cross section with the electric field while the dotted line is the one without an electric field, (b) $F=350$ V/cm, (c) $F=1$ kV/cm, (d) $F=2.5$ kV/cm.

Figure 3 shows the photodetachment cross section when the electric field direction is along the $+z$ axis. Figure 3(a) is the result when the electric field strength is very weak, $F = 25$ V/cm. Under this situation, the influence of the electric field is very small, and the photodetachment cross section approaches the case of the photodetachment of H^- near a metal surface without an electric field.[11] With the increase of the electric field strength, its influence becomes significant, and the oscillating amplitude of the cross section increases gradually, as we can see from Figs. 3(b)–3(d).

The reason for this can be analysed as follows: with the increase of the electric field strength, the force acting on the detached electron becomes strong. When the detached electron leaves the origin and moves along the positive direction of the z axis, it will be attracted back to the origin by the influence of the electric field and the metal surface in a shorter period of time. Thus the stronger the electric field strength, the shorter the period of the closed orbit. From Eq. (16), we can see that when the period T of the closed orbit is short, its contribution to the photodetachment cross section becomes great. At the same time, we can find that no matter what value the electric field is, the upward electric field strengthens the oscillation in the photodetachment. The greater the value is, the stronger the oscillation is.

Next, we consider the case that the direction of the electric field is along the $-z$ axis. The results are shown in Fig. 4, in which figure 4(a) shows the case when the electric field is relatively weak, $F = 50$ V/cm. Under this condition, the electric field force acting on the detached electron cannot counteract the metallic attraction, and the closed orbit of the electron is still along the $+z$ axis and its period is very long. Therefore, its contribution to the cross section is small. The photodetachment cross section still approaches the case of the photodetachment of H^- near a metal surface without an electric field.[11] With the increase of the electric field strength, its influence becomes strong. For $F = 5.14$ kV/cm, its electric field force is able to counteract the metallic attraction.

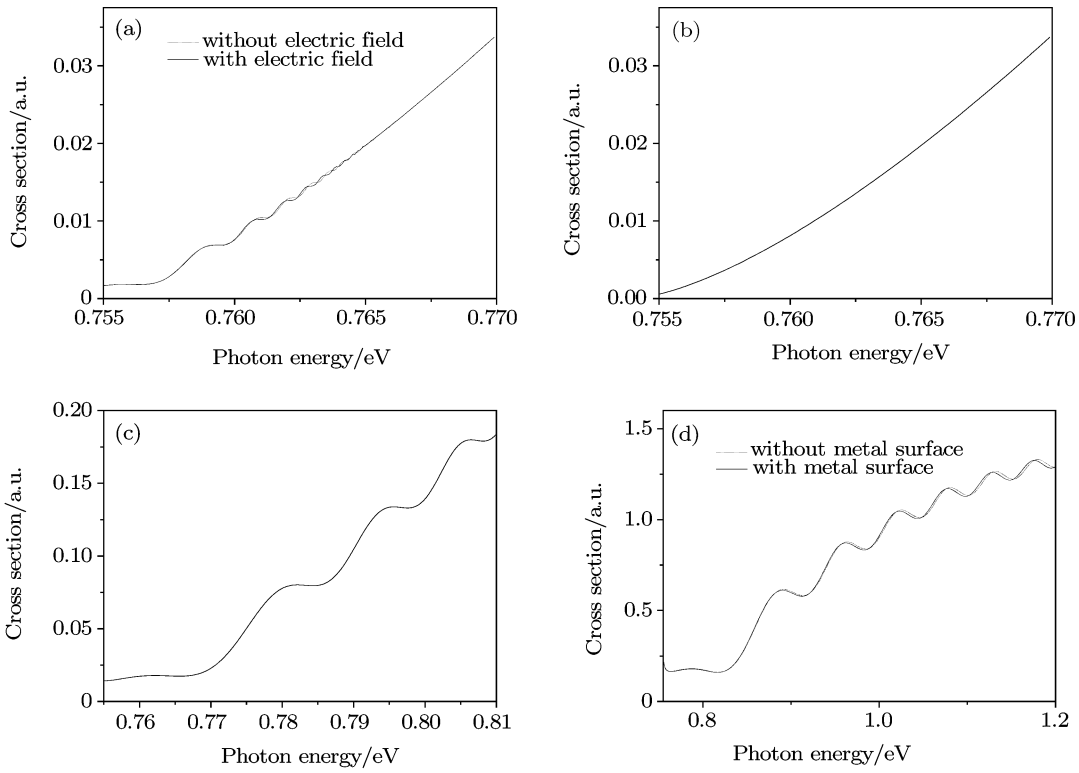


Fig. 4. Photodetachment cross section of H^- in a downward electric field near a metal surface. The distance between the ion and metal surface is 500 a.u. (a) $F = 50$ V/cm, the solid line is the cross section with the electric field while the dotted line is the one without an electric field. (b) $F = 5.14$ kV/cm, the cross section is the same as the one without any external fields. (c) $F = 50$ kV/cm, the oscillation appears in the cross section. (d) $F = 500$ kV/cm, the cross section approaches the case where only the electric field exists.

In this situation, no closed orbit exists, so the photodetachment cross section is the same as the photodetachment of H^- without any external fields, see Fig. 4(b). If we further increase the electric field strength, $F = 50$ kV/cm, the electric field force is larger than the metallic attraction, and a downward closed orbit exists. Oscillation appears again in the cross section, as we can see from Fig. 4(c). If the electric field is extremely strong, its influence becomes dominant and the effect of the metal surface can be neglected. The cross section approximates to the case of the photodetachment of H^- in a downward electric field without a metal surface.[15] The reason for this can be given as follows: when the electric field strength is very strong, the motion of the detached electron is limited to a small region near the hydrogen atom, so that the potential in the Hamiltonian (Eq. (1)) can be approximated as follows:

$$-\frac{1}{4(d+z)}+\frac{1}{4d}-Fz\approx\frac{z}{4d^2}-Fz\approx-Fz. \quad (17)$$

When this approximation is used in Eq. (1), the Hamiltonian becomes identical to the one of the photodetachment of H^- in a static electric field.[14] This is why the curves of the cross section in Fig. 4(d) correspond well with each other.

5. Conclusions

Using the closed-orbit theory, we have investigated the influence of electric field on the photodetachment of H^- near a metal surface. The results suggest that when the direction of the electric field is upward, it strengthens the oscillation in the photodetachment cross section. However, when the direction of the electric field is downward, due to the interaction of the electric field and the metal surface, the detached electron's trajectories change greatly. As the electric field is very weak, the detached electron's trajectories are similar to the case of only a metal surface existing and the photodetachment cross section is nearly the same as the photodetachment of H^- near a metal surface. If the electric field is very strong, the detached electron's motion and the photodetachment cross section approach the case of the photodetachment of H^- in an electric field. Therefore, we can use the electric field to control the photodetachment of H^- near a metal surface. At present, no experiments on this system are available for comparison. We hope that our results will be useful in directing future experimental research on the photodetachment processes of ions in the vicinity of interfaces, cavities and ion traps.[16,17]

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