Electric flux distribution in photodetachment of heteronuclear diatomic molecular negative ion*

Wang De-Hua(王德华)†

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

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The photodetachment of a hetero-nuclear diatomic molecular negative ion is studied by using a two-centre model. An analytic formula is presented for the electron flux distribution of a heteronuclear diatomic molecular negative ion. Taking HF^- as an example, we calculated the electron flux distributions of this ion for various detached electron energies. The results show that the electron flux distributions exhibit oscillatory structures, which are caused by the interference effect between the two nuclei. Besides, the laser light polarization also has a great influence on the electron flux distribution. The oscillation amplitude is the largest when the laser polarization is parallel to the z-axis; when the laser polarization is perpendicular to the z-axis, the oscillation almost vanishes. This study provides a new understanding of the photodetachment of a heteronuclear diatomic molecular negative ion.

Keywords: photodetachment, electron flux, two-centre model, hetero-nuclear diatomic molecular negative ion

PACC: 0365S, 3380E, 3450D

1. Introduction

During the past several decades, the photodetachment of negative ions in various external fields have attracted much attention both theoretically and experimentally.[1−15] In early 1987, Bryant *et al.* observed a ripple-like structure in the photodetachment cross section of H^- in the presence of motional electric fields.[1] Later, Rau and Wong explained this phenomenon by using a frame-transformation theory.[2] Subsequently, many theoretical studies of the photodetachment of H^- in parallel or crossed electric and magnetic fields have been carried out by Fabrikant, Peters and Delos[3] and by other authors.[4−6] It has been found that the photodetachment cross sections of negative ions in an external field display oscillatory structures. Since the photodetachment cross section is proportional to the integrated outgoing electron flux across a large enclosure in which the bound negative ions sit, therefore it is clear that the oscillation in the total cross section of negative ions in an external field reflects the oscillation in the spatial distribution of the electron flux. This predication was also observed experimentally by the photodetachment microscopy. Photodetachment microscopy of negative ions has now served as a very sensitive technique for high accuracy measurements of the electron affinities of atoms or molecules.[16,17] It consists of directly imaging the spatial distribution of electrons photodetached from a negative ion in the presence of a uniform electric field. In contrary to many studies of the negative ions, the research refarding the photodetachment of negative molecular ions in an external field has been carried out very little due to the interference effect of the two nuclei. However, with the development of the molecular photodetachment microscopy technique,[18] the photodetachment of the negative molecular ion in an electric field becomes very important. Recently, Afraq and Du *et al.* have studied the photodetachment of a negative hydrogen molecular ion by using a two-centre model and discussed the interference effect of the two nuclei.[19−21] As to the photodetachment of heteronuclear diatomic molecular negative ions in an external field, Fabrikant studied the photodetachment of an LiF^- in a static electric field by using the Green function method.[22] We studied the electron flux distribution of the photodetachment of HF^- in a static electric field by using the closed orbit theory.[23] In these previous studies, they all considered the photodetachment of a particular molecular negative ion, as to the electron flux distribution of the photodetachment of general hetero-nuclear diatomic molecu-

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

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lar negative ions, no discussion has been made. In the present paper, by using the two-centre model, we give an analytical formula for the photodetachment electron flux distribution of the hetero-nuclear diatomic molecular negative ions. Our formula is universal, which is applicable to the photodetachment of all diatomic molecular negative ions.

2. Theoretical model and method

The schematic diagram of a heteronuclear diatomic molecular negative ion is shown in Fig. 1.

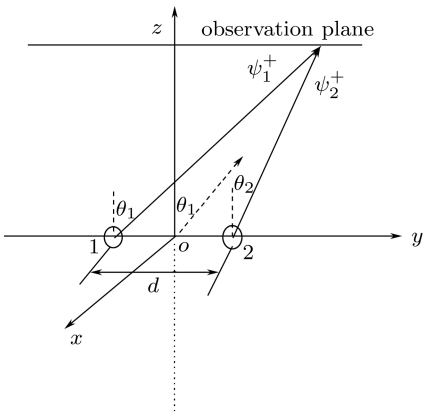


Fig. 1. Schematic diagram for photodetachment of diatomic molecular negative ion system. The two open circles on the y-axis represent the two centres of the negative molecular ion. The observation plane is located at a vertical distance of L away from the two centres, and it is perpendicular to the z-axis, and d is the distance between the two centres. Two outgoing waves, each of which is emitted from its centre, are shown. The laser polarization is in the (θ_L, φ_L) direction.

The photodetachment process can be described as follows: when a heteronuclear diatomic molecular negative ion absorbs photon energies $E_{\rm ph}$, outgoing electron waves are generated. The two nuclei are assumed to interact with each other to an extent sufficient to establish two coherent sources of detached electron. These outgoing waves propagate large distances. Sufficiently far from the molecular ion, the wave propagates according to semiclassical mechanics, and it is correlated with classical trajectories. The detached electron wave at a large distance from the two-centre system can be obtained by using the superposition principle. The detached electron flux far away from the system can be calculated analytically. Due to the interference effect of the two centres, the oscillatory structure appears in the electron flux distribution.

As in Ref. [19], we assume that there is only one active electron in the negative molecular ion system and the active electron is loosely bound by a short-range, spherically symmetric molecular core potential $V_{\rm b}(r)$, where r is the distance between the origin of the system and the active electron. The photo-detached electron wave function satisfies the Schrödinger equation with a source

$$[E - H(r,p)]\psi_{\rm M}^+ = D\psi_{\rm i}, \tag{1}$$

where E is the energy of the detached electron. Suppose that $\hat{\varepsilon}$ is a unit vector in the direction of the laser polarization, then the dipole operator $D = \hat{r}\cdot\hat{\varepsilon}$ will be the projection of electron coordinate on the direction of laser polarization direction. H is the Hamiltonian and $\psi_{\rm i}$ is the initial wave function of the detached electron. For clarity, we take the HF^- as an example. According to the molecular orbit theory, the normalized wave function for the active electron in HF^- can be written as a linear combination of the detached electron wave function of the H^- and F^- at the two centers:[19] $\psi_{\rm i} = c_1\varphi_{1\rm i} + c_2\varphi_{2\rm i}$, where $\varphi_{1\rm i}$ and $\varphi_{2\rm i}$ are the normalized initial wave functions of the H^- and F^-: $\varphi_{1\rm i} = B_1(\,{\rm e}^{{\rm i}k_{\rm b1}r_1}/r_1)$ and $\varphi_{2\rm i} = B_2(\,{\rm e}^{{\rm i}k_{\rm b2}r_2}/r_2)$, respectively, with $B_1 = 0.31552$ and $B_2 = 0.84$ being the normalization constants.[6,24] $k_{\rm b1} = 0.2345$ and $k_{\rm b2} = 0.5$ are related to the binding energies of H^- and F^- by $E_{\rm b} = k_{\rm b}^2/2$ respectively. The c_1 and c_2 are the normalization constants of the HF^-, which can be calculated by using the molecular orbit theory.[25]

For a general case, we assume that the two-center is perpendicular to the z-axis and the laser polarization is along the (θ_L, φ_L) direction. In the negative ion case, an outgoing wave of detached electron centred at the nucleus is generated in the photodetachment process. In the negative molecular ion case, the detached electron wave function is a superposition of detached electron waves generated from the two centres. Let ψ_1^+ and ψ_2^+ be the detached waves from centres 1 and 2 respectively, then the outgoing detached-electron wave from the two-centers can be written as a linear combination given by

$$\psi_{\rm M}^+ = c_1\psi_1^+ + c_2\psi_2^+. \tag{2}$$

Using (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) as the spherical coordinates of the detached electron relative to each centre, we have[6]

$$\psi_1^+(r_1,\theta_1,\phi_1) = U(k,\theta_1,\phi_1)\frac{{\rm e}^{{\rm i}kr_1}}{r_1},$$
$$\psi_2^+(r_2,\theta_2,\phi_1) = U(k,\theta_2,\phi_2)\frac{{\rm e}^{{\rm i}kr_2}}{r_2}. \tag{3}$$

The factors $U(k,\theta_1,\phi_1)$and $U(k,\theta_2,\phi_2)$ for the laser polarization along the (θ_L,φ_L) direction can be written as

$$U(k,\theta_1,\phi_1) = \mathrm{i}\frac{4kB_1}{(k_{\mathrm{b}1}^2+k^2)^2} f(\theta_1,\phi_1;\theta_L,\phi_L),$$
$$U(k,\theta_2,\phi_2) = \mathrm{i}\frac{4kB_2}{(k_{\mathrm{b}2}^2+k^2)^2} f(\theta_2,\phi_2;\theta_L,\phi_L). \quad (4)$$

The angular factors $f(\theta_1,\phi_1;\theta_L,\phi_L)$ and $f(\theta_2,\phi_2;\theta_L,\phi_L)$ represent the dependence of the detached-electron wavefunction on outgoing directions (θ_1,ϕ_1) and (θ_2,ϕ_2), which can be written as[21]

$$\begin{aligned} & f(\theta_1,\phi_1;\theta_L,\phi_L) \\ =\ & \cos\theta_1\cos\theta_L + \sin\theta_1\sin\theta_L\cos(\phi_1-\phi_L), \\ & f(\theta_2,\phi_2;\theta_L,\phi_L) \\ =\ & \cos\theta_2\cos\theta_L + \sin\theta_2\sin\theta_L\cos(\phi_2-\phi_L). \end{aligned} \quad (5)$$

The detached electron wave function from the negative molecular ion can be written as:

$$\begin{aligned} & \psi_{\mathrm{M}}^{+}(r,\theta,\phi) \\ =\ & \mathrm{i}\left[c_1\frac{4kB_1}{(k_{\mathrm{b}1}^2+k^2)^2} f(\theta_1,\phi_1;\theta_L,\phi_L)\frac{\mathrm{e}^{\mathrm{i}kr_1}}{r_1}\right. \\ & \left. + c_2\frac{4kB_2}{(k_{\mathrm{b}2}^2+k^2)^2} f(\theta_2,\phi_2;\theta_L,\phi_L)\frac{\mathrm{e}^{\mathrm{i}kr_2}}{r_2}\right], \end{aligned} \quad (6)$$

where (r,θ,ϕ) is the spherical coordinates of the detached electron with respect to the origin. When the detached electrons are measured in a region far away from the two centres, distances r_1 and r_2 are much greater than the distance between the two centres d, then the above formula can be simplified further. As in Ref. [19], we use $r_1 \approx r + (d\sin\theta\sin\varphi)/2$ and $r_2 \approx r - (d\sin\theta\sin\varphi)/2$ for the phase terms and in all other places use $r_1 \approx r_2 \approx r$ and $\theta_1 \approx \theta_2 \approx \theta$. With these approximations, equation (6) becomes

$$\begin{aligned} & \psi_{\mathrm{M}}^{+}(r,\theta,\phi) \\ =\ & \mathrm{i}\frac{\mathrm{e}^{\mathrm{i}kr}}{r} f(\theta,\phi;\theta_L,\phi_L) \\ & \times\left[D_1\,\mathrm{e}^{\mathrm{i}(kd\sin\theta\sin\varphi/2)} + D_2\,\mathrm{e}^{-\mathrm{i}(kd\sin\theta\sin\varphi/2)}\right], \end{aligned} \quad (7)$$

in which $D_1 = 4kB_1c_1/(k_{\mathrm{b}1}^2+k^2)^2$, $D_2 = 4kB_2c_2/(k_{\mathrm{b}2}^2+k^2)^2$, and the angular factor $f(\theta,\phi;\theta_L,\phi_L)$ is

$$\begin{aligned} & f(\theta,\phi;\theta_L,\phi_L) \\ =\ & \cos\theta\cos\theta_L + \sin\theta\sin\theta_L\cos(\phi-\phi_L). \end{aligned} \quad (8)$$

For a given observation plane perpendicular to the z axis, the electron flux in that plane is defined as[19]

$$\boldsymbol{j}(r,\theta,\varphi) = \frac{\mathrm{i}}{2}(\psi_{\mathrm{M}}^{+}\nabla\psi_{\mathrm{M}}^{+*} - \psi_{\mathrm{M}}^{+*}\nabla\psi_{\mathrm{M}}^{+}) \ . \quad (9)$$

Substituting Eq. (9) into the above formula, the electron flux is shown to exhibit a typical two-term interference pattern. The detached electron flux in the radial direction at large r is $j_r(r,\theta,\varphi) = (\mathrm{i}/2)(\psi_{\mathrm{M}}^{+}\partial\psi_{\mathrm{M}}^{+*}/\partial r - \psi_{\mathrm{M}}^{+*}\partial\psi_{\mathrm{M}}^{+}/\partial r)$. Substituting expression (7) into the above formula, we have

$$\begin{aligned} j_r(r,\theta,\varphi) =\ & \frac{k}{r^2} f^2(\theta,\phi;\theta_L,\phi_L)[D_1^2+D_2^2 \\ & + 2D_1D_2\cos(kd\sin\theta\sin\phi)]. \end{aligned} \quad (10)$$

In order to obtain the flux in the observation plane, we project the flux in expression (10) in the normal direction of the plane:

$$j_z(r,\theta,\varphi) = j_r(r,\theta,\varphi)\hat{r}\cdot\hat{n} \ . \quad (11)$$

Since $\hat{r}\cdot\hat{n} = \cos\theta$, we have

$$\begin{aligned} & j_z(r,\theta,\varphi) \\ =\ & \frac{k}{r^2} f^2(\theta,\phi;\theta_L,\phi_L)[D_1^2+D_2^2 \\ & + 2D_1D_2\cos(kd\sin\theta\sin\phi)]\cos\theta. \end{aligned} \quad (12)$$

3. Results and discussion

For the laser that is polarized in the z direction perpendicular to the molecular axis, the distance between the observation plane and the two centres is L, then $\theta_L = \phi_L = 0$, $f(\theta,\phi;\theta_L,\phi_L) = \cos\theta$. In the above formula, $\cos\theta = L/r$, and $\sin\theta\sin\phi = y/r$. Then the detached electron flux in the z-direction is

$$\begin{aligned} & j_z(r,\theta,\varphi) \\ =\ & \frac{kL^3}{(x^2+y^2+z^2)^{5/2}}\left[D_1^2+D_2^2\right. \\ & \left. + 2D_1D_2\cos\left(\frac{kdy}{\sqrt{x^2+y^2+z^2}}\right)\right]. \end{aligned} \quad (13)$$

By using expression (13), we calculate the photodetachment electron flux distribution of HF^- on the $x = 0$ line in a given observation plane for different electron energies, the distance between the two centres of HF^- is close to the equilibrium distance of the HF molecule $d = 1.7329$ a.u. The distance between the molecular ion and the observation plane is $L = 1000$ a.u. The result is given in Fig. 2.

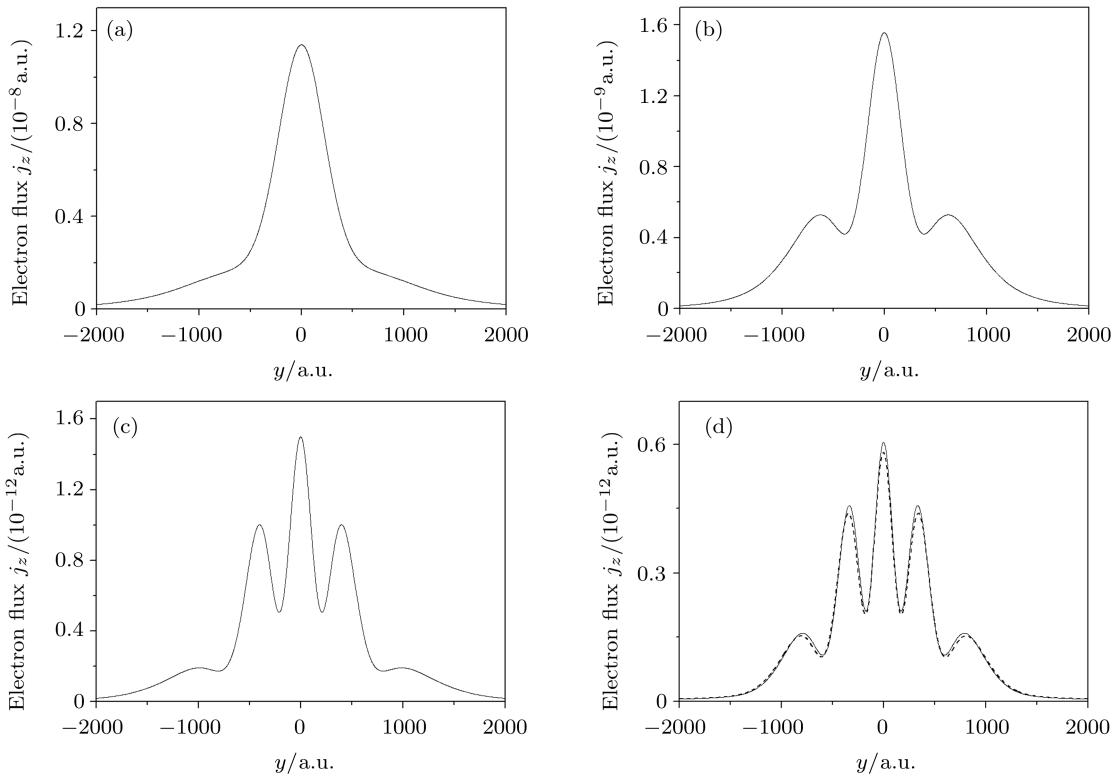


Fig. 2. Electron flux distribution for the photodetachment of HF^-. The distance between the two centres of the HF^- is $d = 1.732$ a.u. The distance between the molecular ion and the observation plane is $L = 1000$ a.u. The electron energies are as follows: (a) $E = 179.05$ eV; (b) $E = 402.85$ eV; (c) $E = 1119.03$ eV; (d) $E = 1616.41$ eV.

From this figure it follows that with the increase of the detached electron energy, the oscillations in the electron flux become much more complicated. The peaks due to the interference of detached electron from the two centres are clearly visible. For example, for energy $E = 179.05$ eV, there occurs only one peak. As energy increases to 1119.03 eV, there appear three peaks caused by the interference effect of the two centres. In our present work, due to the weak interaction between the HF molecule and the detached electron, the outgoing detached-electron wave function has been written as a linear combination given by expression (2). Strictly speaking, this is only an approximate expression. For the heteronuclear diatomic molecular negative ions, due to the coupling among different states, the wave function should be written in a multi-channel coupling form. By using the multi-channel couple wave function, we calculate the photodetachment electron flux distribution of HF^- at the energy $E = 1616.41$ eV, the result is shown by the dash line in Fig. 2(d). From this figure it follows that the two results are in good agreement with each other, which suggests that our approximation is suitable.

Next, we calculate the electron flux of HF^- for a given detached electron energy in different observation planes, see Fig. 3.

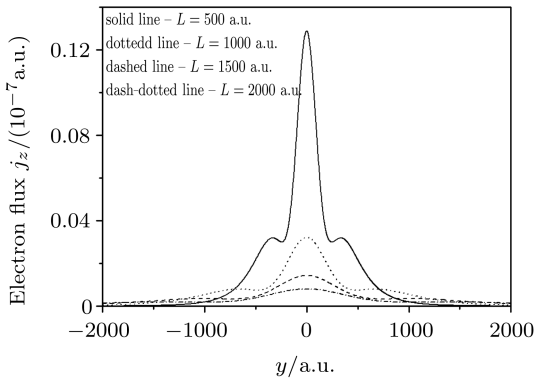


Fig. 3. Electron flux distributions for the photodetachment of HF^- in different observation planes. The distance between the two centres of the HF^- is $d = 1.732$ a.u. The electron energy is $E = 300$ eV. The distances between the molecular ion and the observation plane L are 500 a.u. (solid line), 1000 a.u. (dot line), 1500 a.u. (dash line), 2000 a.u. (dash-dot line).

The results suggest that with the increase of the distance between the molecular ion and observation

plane, the oscillation in the electron flux distribution becomes decreased, which can be interpreted as follows: when the observation plane is far from the molecular ion, the strengths of the outgoing waves in the observation plane, emitted from the two centres, are small, therefore, the interference effect caused by the two nuclei becomes damped. Finally, we discuss the laser polarization effect on the electron flux distribution of HF^-, see Fig. 4, where the electron flux distributions for several values of polarization angle θ_L, azimuth angle $\phi_L = \pi/2$, $d = 1.732$ and $L = 1000$ a.u. are shown for comparison.

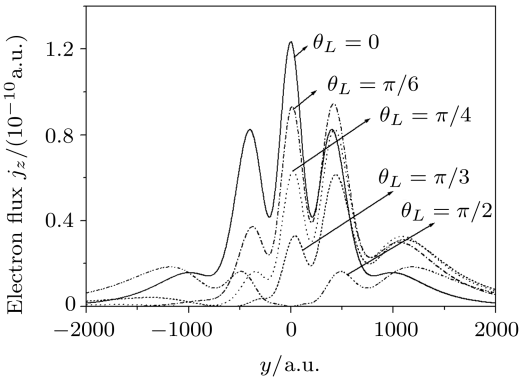


Fig. 4. Laser polarization effect on the photodetachment electron flux of HF^-. The distance between the two centres of the HF^- is $d = 1.732$ a.u. The electron energy is $E = 1$ MeV. The distance between the molecular ion and the observation plane L is 1000 a.u., i.e. $L = 1000$ a.u. The laser polarization angles relative to the z-axis, θ_L, are 0 (solid line), $\pi/6$ (dash-dot line), $\pi/4$ (dot line), $\pi/3$ (short dash line), and $\pi/2$ (dash-dot-dot line).

This figure suggests that the oscillation is the largest when the laser polarization is parallel to the z axis, i.e. $\theta_L = 0$. As the polarization angle θ_L increases, the amplitude of the oscillation in the electron flux decreases. When the laser polarization is perpendicular to the z-axis, i.e. $\theta_L = \pi/2$, the oscillation almost vanishes.

4. Conclusions

We studied the photdetachment electron flux of heteronuclear diatomic molecular negative ions by using the two-centre model. An analytical formula for the electron flux distribution is derived. Our formula is universal and applicable to all the diatomic molecular negative ions. Taking the HF^- as an example, we calculated the electron flux distribution in a given observation plane. The results show that the outgoing electron waves, each of which is emitted from its centre produce oscillations in the electron flux distributions. Besides, the laser polarization also affects the electron flux distribution. The oscillations in the electron flux almost disappear as the laser polarization angle increases from 0 to $\pi/2$ relative to the z-axis. Presently, no experiments on the photodetachment of HF^- have been carried out. We expect our results to guide the future experiment research on the molecular photodetachment microscope.

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