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Charge Exchange Processes in the Scattering of Li^+ off Narrow Band Insulator (KF) Surface in the Presence of Laser Field

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***Abstract:* -** By using one-electron Hamiltonian for describing the dynamics of interaction between species and solid surface in the scattering process, in the presence of a monochromatic electromagnetic field (laser field), we present detailed theoretical treatment and model calculation to describe the surface-ion charge exchange mechanism. We apply our treatment to the scattering of Li^+ from KF insulator surface. Our application ensure that the species charge state can be controlled by the laser field.

Keywords: *scattering process, surface-ion charge exchange processes, monochromatic electromagnetic field, laser frequency, laser coupling strength.*

I. INTRODUCTION

Laser assisted and laser induced processes in the gas-phase-metal surface slow collisions play an important role in plasma physics. With lasers, chemists have begun to control chemical reaction dynamics in gas - phase reactions and reactions occurring at the gas - solid interface. Lasers have been used to study state - selected reactions, new reaction pathways and transition - state spectroscopy.

The electromagnetic field associated with the laser beam has four controllable parameters: frequency, polarization, intensity, and propagation vector. By varying these parameters, as well as the coherence of the radiation, experimentalists create a flexible stimulator and probe of chemical dynamics [1].

The interaction of laser with matter in homogeneous systems has been extensively studied for the past years [2-4]. However, for heterogeneous systems (e.g. gaseous atoms near or adsorbed on a solid surface) the laser stimulated surface phenomena (adsorption, dissociation, migration and reactions) involving both multiphoton and multiphonon processes have been recently studied and investigated for many systems extendedly [5-7]. (For more details see references [8,9] and references there in).

Theoretical techniques for describing laser- stimulated surface processes in a vacuum and at a gas-surface interface are presented in ref.[10]. For adspecies-surfaces systems, the laser excitation of vibrational degrees of freedom was considered, and quantum- mechanical and classical models and also an "almost first principles" treatment of the competition between multiphoton absorption and multiphonon relaxation were discussed. The laser excitation of electronic degrees of freedom was considered with respect to surface states of semiconductors and metals, for the predissociation of diatomic adspecies on metal substrates, for ionization, and for resonance fluorescence of a gaseous atom near a metal. In connection with gas- surface interactions, the influence of laser radiation on diffraction patterns and energy transfer in atom- surface scattering was explored. Collisional ionization and ion neutralization in the presence of laser radiation were discussed. The roles of partial pressure and surface converge in laser-stimulated surface processes were analyzed.

One electron resonant and two electron Auger processes in slow collisions of atoms (ions) with a metal surface in the presence of a laser field have been considered in ref.[11]. The Hamiltonian of the system atom + surface + laser field was written in the form,

$$H(t) = H_o + V(t)$$

where, $V(t)$ contains both the atom – metal interaction and the interaction with the laser field. The total wave function, which satisfies the time dependent Schrodinger equation, was expanded in terms of orthonormal basis set for electron states in the metal and in the atom. They obtained a system of coupled ordinary equations for the amplitudes of these processes. Their theoretical considerations led them to believe that laser-assisted processes at surfaces should occur at the same magnitudes of the laser- field intensity (~ 10^{16} W/m^2) as those in corresponding atomic- collision processes.

In this work, our aim is to use our earlier develop theoretical treatment [8,9] which is related to the interaction of laser field with atom-surface system in the case of scattering. The laser field is incorporated into the surface-adspecies system Hamiltonian, which is the first requirement to describe the laser-assisted charge transfer processes. The theoretical treatment for the scattering of atoms (or ions) from solid surfaces in the presence of laser field (incorporating all its effects) is briefly out line in section two. Our applications to real systems Li^{+}-KF are investigated and highlighted in section three. While, very important conclusions about laser ionization are reported in section four.

II. FORMALISM

In this section we briefly present the earlier developed theoretical treatment [8,9]. To incorporate the laser field into the surface-ion neutralization equations of motion, the one-electron formalism is extended to include an additional term in the system Hamiltonian that needed to describe the laser-assisted charge transfer processes.

2.1 The System Hamiltonian

We incorporate the laser field effects by introducing the vector potential $\overline{A}(\bar{r},t)$ of a monochromatic electromagnetic field into the system one-electron Hamiltonian as follows,

$$\hat{H}=\frac{1}{2m}\left(\overline{P}+\frac{e}{c}\overline{A}(\bar{r},t)\right)^{2}+V_{M}(\bar{r})+V_{A}\left(\left|\bar{r}-\overline{R}_{A}\right|\right)+V_{pol}(\bar{r},t)-e\varphi \tag{1}$$

where, $\overline{P}=-i\hbar\overline{\nabla}$ is the momentum of an electron in the metal-atom system. $\overline{A}(\bar{r},t)$ and φ are the vector and scalar potentials respectively.

The vector potential $\overline{A}$ of the laser field of frequency ω_L and wave vector $k=2\pi/\lambda$ (λ being the radiation wavelength), for linear polarization, is given by[8,9],

$$\overline{A}(\bar{r},t)=\hat{e}A_{o}\cos\left(\omega_{L}t-\bar{k}\cdot\bar{r}+\delta\right)\ ;\ A_{o}=cE_{o}/\omega_{L} \tag{2}$$

with, $\hat{e}$ is the unit vector along the direction of the vector potential, δ is the phase angle, E_o and c are the field amplitude and the light speed respectively.

As this field has no source in the vicinity of the atom-solid surface system, it may be derived according to Maxwell's theory from the vector and scalar potentials, $\overline{A}(\bar{r},t)$ and φ respectively, which satisfy the following equations [12],

$$\overline{\nabla}\cdot\overline{A}(\bar{r},t)=0\quad ;\quad \varphi=0\quad ;\quad \overline{E}=-d\overline{A}(\bar{r},t)/dt \tag{3}$$

The different contributions to the potential field of an electron in the atom-solid surface system are the following:

1. The field of the semi-infinite metal $V_M(\bar{r})$ extends from $z=-\infty$ to $z=0$ ($z=0$ being the metal-vacuum interface position).
2. The field of isolated atom $V_A\left(\left|\bar{r}-\overline{R}_A(t)\right|\right)$ is centered at $\overline{R}_A(t)$.
3. The polarization term $V_{pol}(\bar{r},t)$ which represents the interaction of the electron with the charge induced on the metal surface by the presence of the atom.

Then, our one-electron Hamiltonian reads,

$$\hat{H}=\frac{P^{2}}{2m}+V_{M}(\bar{r})+V_{A}\left(\left|\bar{r}-\overline{R}_{A}\right|\right)+V_{pol}(\bar{r},t)+\frac{e}{2mc}\overline{A}(\bar{r},t)\cdot\overline{P}+\frac{e^{2}}{2mc^{2}}A^{2}(\bar{r},t) \tag{4}$$

from eq.(4) one can conclude that the study of laser-assisted surface-ion neutralization (LASIN) requires the addition of other two terms to the one-electron Hamiltonian, that describe the coupling between the ion and the solid surface orbital due to their interaction with the electromagnetic field of the laser radiation. These terms are denoted by,

$$V_{L}(\bar{r},t)=(e/2mc)\overline{A}(\bar{r},t)\cdot\overline{P}+(e^{2}/2mc^{2})A^{2}(\bar{r},t) \tag{5}$$

2.2 The Equations of Motion Derivation

The energy eigenvalues and the corresponding eigenfunctions of the electron states of the semi-infinite metal are denoted by E_μ and $\Psi_\mu(\bar{r},t)$ respectively (with μ stands for a complete set of quantum numbers), and that for the single atomic orbital by E_A^{∞} and $\Psi_A(\bar{r},t)$ respectively. The time development of the jth orbital $(j=1,2,\ldots,N)$ of Slater determinant is determined by solving Schrödinger equation,

$$i\hbar d\Psi_{j}(\bar{r},t)/dt=\hat{H}\Psi_{j}(\bar{r},t) \tag{6}$$

Then, we seek a solution for the above equation in the following form,

$$\Psi_j(\bar{r},t)=\sum_{\mu}C_{\mu j}(t)\Psi_\mu(\bar{r},t)+C_{Aj}(t)\Psi_A(\bar{r},t)$$

(7)

Which on substituting it in Schrodinger equation one gets,

$$\begin{aligned}
&i\hbar\sum_{\nu}\dot{C}_{\nu j}(t)\Psi_\nu(\bar{r},t)+i\hbar\dot{C}_{Aj}(t)\Psi_A(\bar{r},t)= \\
&\qquad\sum_{\nu}C_{\nu j}(t)\left[V_A\left(\left|\bar{r}-\bar{R}_A\right|\right)+V_{pol}(\bar{r},t)+V_L(\bar{r},t)\right]\Psi_\nu(\bar{r},t) \\
&\qquad+C_{Aj}(t)\left[V_M(\bar{r})+V_{pol}(\bar{r},t)+V_L(\bar{r},t)\right]\Psi_A(\bar{r},t)
\end{aligned} \tag{8}$$

Then, multiplying with $\Psi^*_\mu(\bar{r},t)$ or with $\Psi^*_A(\bar{r},t)$ and integrating over all space. Because our interest in the charge transfer between the solid surface and the projectile, we ignore any coupling among the states in the surface energy band and use the following matrix elements,

$$\begin{aligned}
&\int\Psi^*_A(\bar{r},t)V_{pol}(\bar{r},t)\Psi_A(\bar{r},t)d\tau=\varepsilon_{im}(t)\ ;\ \int\Psi^*_\mu(\bar{r},t)V_L(\bar{r},t)\Psi_A(\bar{r},t)d\tau=\tilde{W}_{\mu A}(t) \\
&\int\Psi^*_\mu(\bar{r},t)V_M(\bar{r})\Psi_A(\bar{r},t)d\tau=\tilde{V}_{\mu A}(t)\ ;\ \int\Psi^*_A(\bar{r},t)V_A\left(\left|\bar{r}-\bar{R}_A\right|\right)\Psi_\mu(\bar{r},t)d\tau=\tilde{V}_{A\mu}(t)
\end{aligned} \tag{9}$$

Notably, some of the integrals are disregarded, since this approximation is common to all existing theories based on the Hamiltonian in eq. (1) [8,9,13], while all other integrals are dominant. $\varepsilon_{im}(t)$ is the shift in the energy level of the atomic orbital due to charge polarization on the surface which is usually approximated by an image shift. Accordingly, the equations of motion for the ion-surface scattering problem are,

$$\begin{aligned}
&\dot{C}_{\mu j}(t)=-\frac{i}{\hbar}C_{Aj}(t)\left[\tilde{V}_{\mu A}(t)+\tilde{W}_{\mu A}(t)\right] \\
&\dot{C}_{Aj}(t)=-\frac{i}{\hbar}\varepsilon_{im}(t)C_{AJ}(t)-\frac{i}{\hbar}\sum_{\mu}C_{\mu j}(t)\left[\tilde{V}_{A\mu}(t)+\tilde{W}_{A\mu}(t)\right]
\end{aligned} \tag{10}$$

By assuming $j=\mu'$ be the orbital which originates from a metal state, we get the following equations,

$$\begin{aligned}
&\dot{C}_{\mu\mu'}(t)=-\frac{i}{\hbar}C_{A\mu'}(t)\left[\tilde{V}_{\mu A}(t)+\tilde{W}_{\mu A}(t)\right] \\
&\dot{C}_{A\mu'}(t)=-\frac{i}{\hbar}\varepsilon_{im}(t)C_{A\mu'}(t)-\frac{i}{\hbar}\sum_{\mu}C_{\mu\mu'}(t)\left[\tilde{V}_{A\mu}(t)+\tilde{W}_{A\mu}(t)\right]
\end{aligned} \tag{11}$$

which should be solved with the initial conditions, $C_{\mu\mu'}(t_o)=\delta_{\mu\mu'}\ ;\ C_{A\mu'}(t_o)=0$, to get

$$\begin{aligned}
&\dot{C}_{A\mu'}(t)=-\frac{i}{\hbar}\varepsilon_{im}(t)C_{A\mu'}(t)-\frac{i}{\hbar}\left[\tilde{V}_{A\mu'}(t)+\tilde{W}_{A\mu'}(t)\right] \\
&-\frac{1}{\hbar^2}\sum_{\mu}\left[\tilde{V}_{A\mu'}(t)+\tilde{W}_{A\mu'}(t)\right]\int_{t_o}^{t}\left[\tilde{V}_{\mu A}(t')+\tilde{W}_{\mu A}(t')\right]C_{A\mu'}(t')dt'
\end{aligned} \tag{12}$$

The ion neutralization probability at time t is given by [13,14],

$$n_A(t)=\sum_{\mu'(occ.)}\left|C_{A\mu'}(t)\right|^2 \tag{13}$$

The summation is over all occupied solid surface states. Then, we define[8,9,13],

$$\begin{aligned}
&C_{A\mu'}(t)=V_{\mu}C(E,t)\\
&\tilde{V}_{A\mu}(t)+\tilde{W}_{A\mu}(t)=V\mu e^{-i\left(E_{\mu}-E_{A}^{\infty}\right)t}\,H(t)\\
&H(t)=V(t)+W(t)\\
&\rho_{s}(E)=\sum_{\mu}\left|V_{\mu}\right|^{2}\delta\left(E_{\mu}-E\right)
\end{aligned} \qquad 14)$$

where, $\rho_s(E)$ defines the surface density of states. Then, eqs. (12) and (13) become,

$$\begin{aligned}
\dot{C}(E',t)=&-\frac{i}{\hbar}\varepsilon_{im}(t)C(E',t)-\frac{i}{\hbar}e^{-i\left(E'-E_{A}^{\infty}\right)t}H(t)\\
&-\frac{1}{\hbar^{2}}H(t)\int_{t_\circ}^{t}dt'\,H(t')e^{iE_{A}^{\infty}\left(t-t'\right)}\int dE\,\rho_{s}(E)\,e^{-iE(t-t')}\,C(E',t)
\end{aligned}$$

(15)

$$n_A(t)=\int\rho_s(E')\left|C(E',t)\right|^2dE' \qquad (16)$$

If we put $\rho_s(E)=\overline{\rho}$ (as constant, $\overline{\rho}=1/4\beta$), then the remaining energy integral is simply the definition of the delta function as [15], $\int e^{-iE(t-t')}\,dE=2\pi\delta(t-t')$. And finally we have,

$$\dot{C}(E',t)=\left[-\frac{i}{\hbar}\varepsilon_{im}(t)-\frac{\overline{\rho}}{\hbar^{2}}\left|H(t)\right|^{2}\right]C(E',t)-\frac{i}{\hbar}H(t)e^{-i(E'-E_{A}^{\infty})t} \qquad (17)$$

Then the last term in eq. (15) being, $e^{i2\beta\gamma t}\,H(t)\int_{t_\circ}^{t}H(t')\,C(E,t')dt'$. So, eq.(15) becomes

$$\dot{C}(E',t)=-\frac{i}{\hbar}e^{-i(E-E_{A}^{\infty})}H(t)-\frac{1}{\hbar^{2}}e^{i2\beta\gamma t}H(t)\int_{t_\circ}^{t}e^{-i2\beta\gamma t'}H(t')C(E,t)dt \qquad (18)$$

All the system energies are measured with respect to Fermi level and the atomic unit is used throughout text.

Under the assumption that the wavelength of the electromagnetic radiation is long when compared with the size of the electron orbital, i.e. $\lambda/\Delta r>>1$ or $k\Delta r<<1$ [16] we obtain,

$$\overline{A}(t)=\hat{e}A_{o}\cos\left(\omega_{L}t+\delta'\right) \qquad (19)$$

Then the matrix element $H(t)$ in eq.(14) can be read as, $H(t)=V(t)+eE_oW(t)$.

Because of the localized nature of the atomic orbital, they overlap substantially only when the ion is close to the surface, and $W(t)$ has the same qualitative behavior as that of $V(t)$. Thus the simplest model for $W(t)$ is the analog to [14],

$$V(t)=V_{o}\,e^{-\alpha_{A}u|t|}\;,W(t)=W_{o}\,e^{-\alpha_{A}u|t|}\left[e^{-i\omega_{L}t-i\delta}+e^{i\omega_{L}t+i\delta}\right],\ \alpha_{A}=\sqrt{2\left|E_{A}^{\infty}\right|}$$

(20) with, V_o and W_o are the hopping and laser coupling strengths respectively and u is the normal component of the species velocity.

In order to gain more insight and to check the applicability of our treatment, we apply it to the scattering of Li^{+} from the insulator surface KF.

III. RESULTS, DISCUSSION AND CONCLUSIONS

The physical situation we are considering here does not entail several competing processes such as emission of electrons, desorption and migration of adsorbed species. To avoid dealing with these processes, the laser frequency is required not to be in resonance with adatom vibration and phonon modes. These processes can be controlled experimentally through the atom beam and the laser radiation. In our treatment, we use a suitable combination of the two effective parameters. The electromagnetic field associated with laser beam has two controllable parameters, these are laser frequency and laser power, these parameters are selected to avoid the above - mentioned processes.

To determine the size of laser effect on the neutralization process of ion scattered from solid surface with narrow energy band, we have performed calculations for the neutralization probabilities for the system Li^+ scattered from insulator surface KF using eq. (18) which is solved numerically. KF is an insulator with narrow valence band width equals to 1.5 eV (i.e. $\beta = 0.01378 a.u.)$ with α lies on -0.4189 a.u. (-11.457 eV) (see fig. (1)). The Li^+ projectile atomic energy level lies at -5.39 eV and the coupling strength is assumed to 0.875 eV, i.e. the atomic level position E_A^∞ is facing an empty band and we will brought the component $E_A - \hbar\omega_L$ within the occupied band by using suitable value of laser frequency.

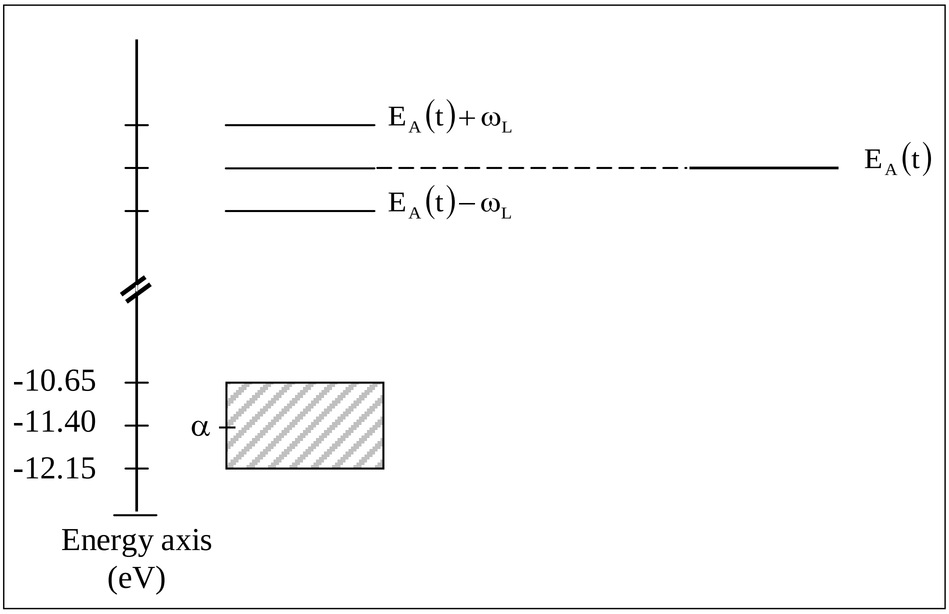
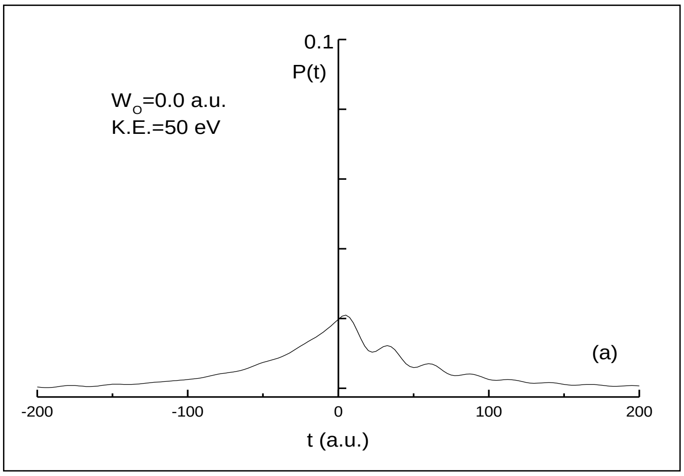
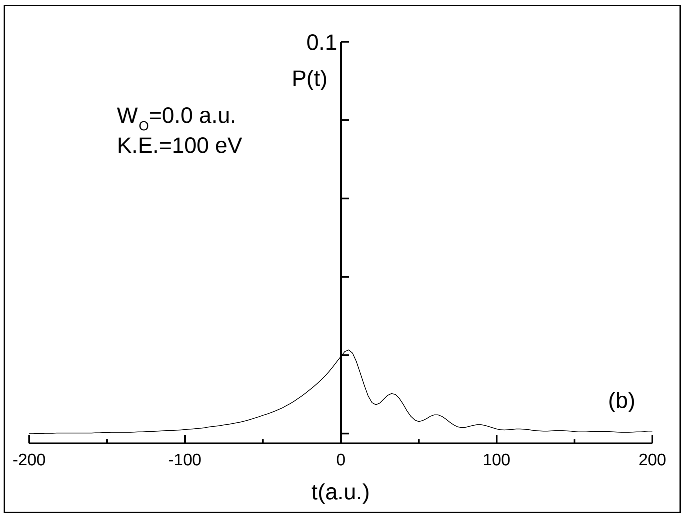


Fig. (1):The valence band electronic structure of KF and the atomic level position of Li with respect to vacuum level $(E = 0)$.

For comparison, we plot the neutralization probabilities $n_A(t)\,(= P(t))$ as a function of time in figs.((2)-(5)) in the absence of laser effect $(W_o = 0)$ and in the presence of it with $W_o = 0.001, 0.005, 0.01 a.u.$ for three different values of ion kinetic energies 50, 100, 200 eV. The laser frequency is taken to be 0.2207a. u. ($\hbar\omega = 6.005$ eV) so as to match the energy difference between the ion's valance level and the band centre α.





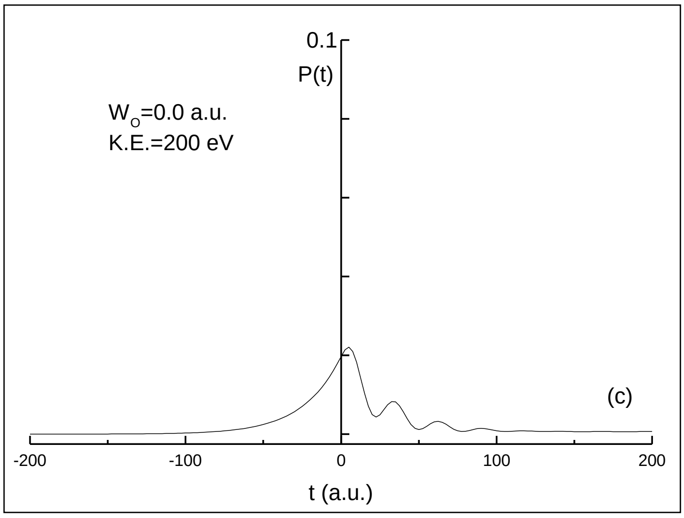


Fig.(2):The neutralization probability of Li^{+} as a function of time in the absence of laser field for three different values of ion kinetic energies.

In the absence of laser field, there is essentially no neutralization of Li^{+} even within low kinetic energies and even in the closest approach at the outgoing trajectory as it faces empty energy band levels. If the laser field is switched on, one can observe ion neutralization which can be attributed to laser-induced process by bringing one of the level component $\mathrm{E}_{\mathrm{A}}(\mathrm{t})-\hbar\omega_{\mathrm{L}}$ within the occupied band.

Figs. (3),(4) and (5) clarify many points of interest. $\mathrm{P}(\mathrm{t})$ increases for all times in the presence of laser field. If one compares between the laser parameters effects and the system parameters effects, one can conclude that the former is dominated. The oscillation behavior near the surface may be attributed to the ion projectile low velocity, since there will be enough time for the electron to transfer between atomic level and band levels especially at 50 eV. But if we keep in mind that the surface energy band is narrow, the oscillatory nature of $\mathrm{P}(\mathrm{t})$ may be understood qualitatively on the basis of the two-level model which gives the same results as our model with either zero band width or with a single band level.

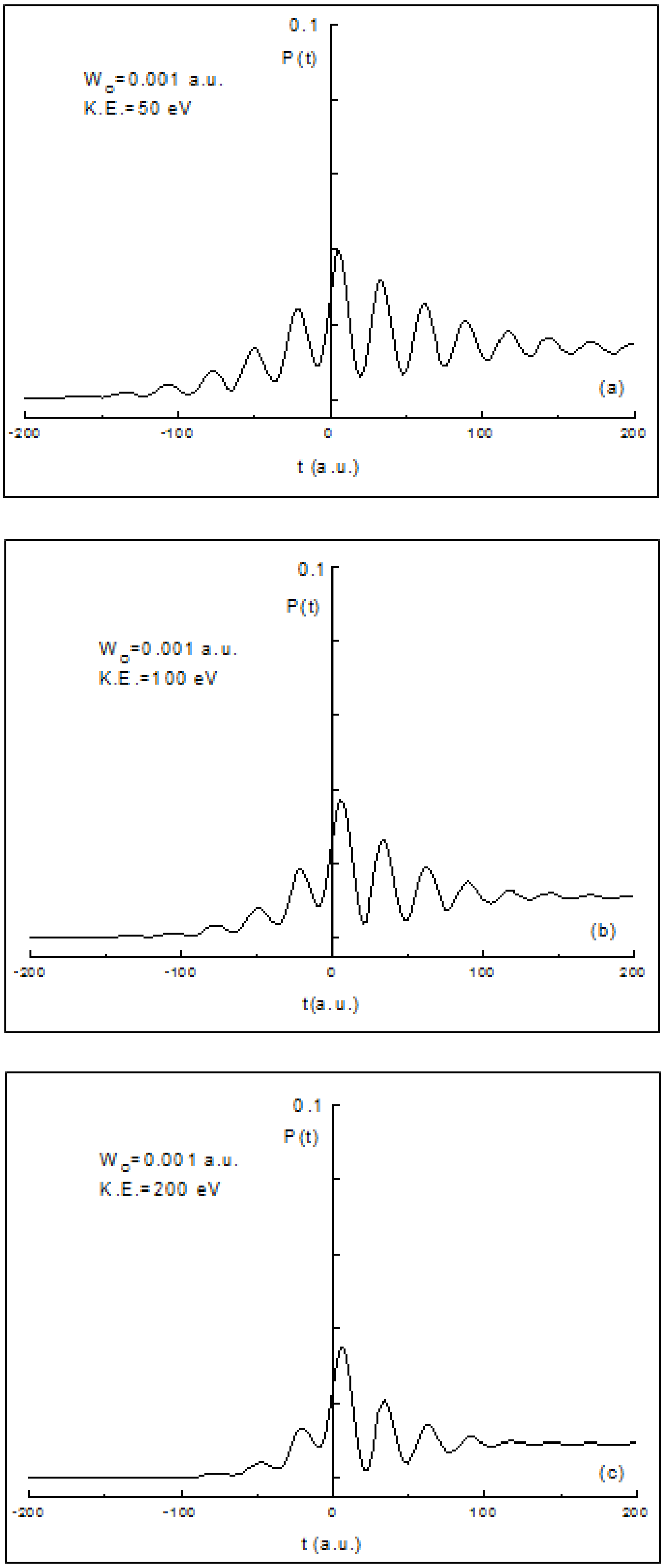


Fig.(3):The neutralization probability of Li^+ as a function of time in the presence of laser field with $W_o = 0.001\,\mathrm{a.u.}$ for three different values of ion kinetic energies.

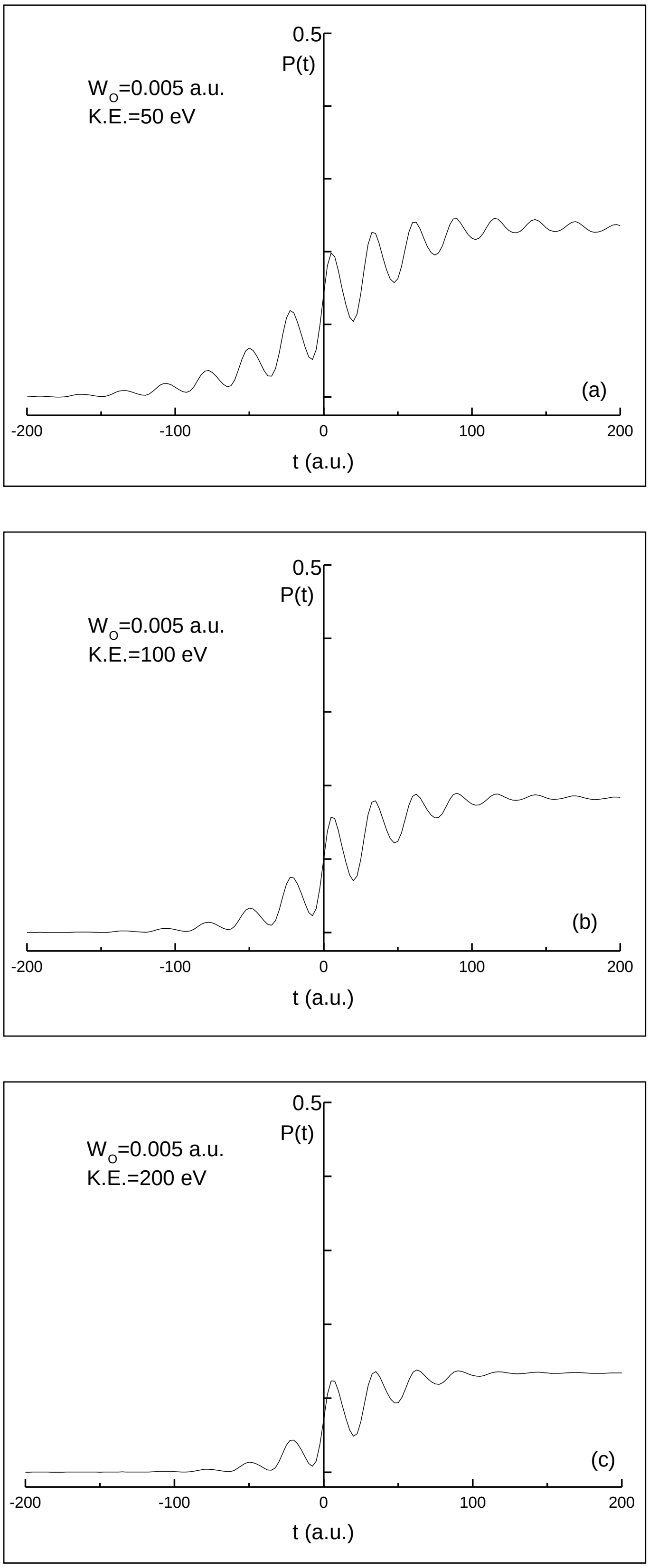


Fig.(4):The neutralization probability of Li^{+} as a function of time in the presence of laser field with $\mathrm{W_o} = 0.005\ \mathrm{a.u.}$ for three different values of ion kinetic energies.

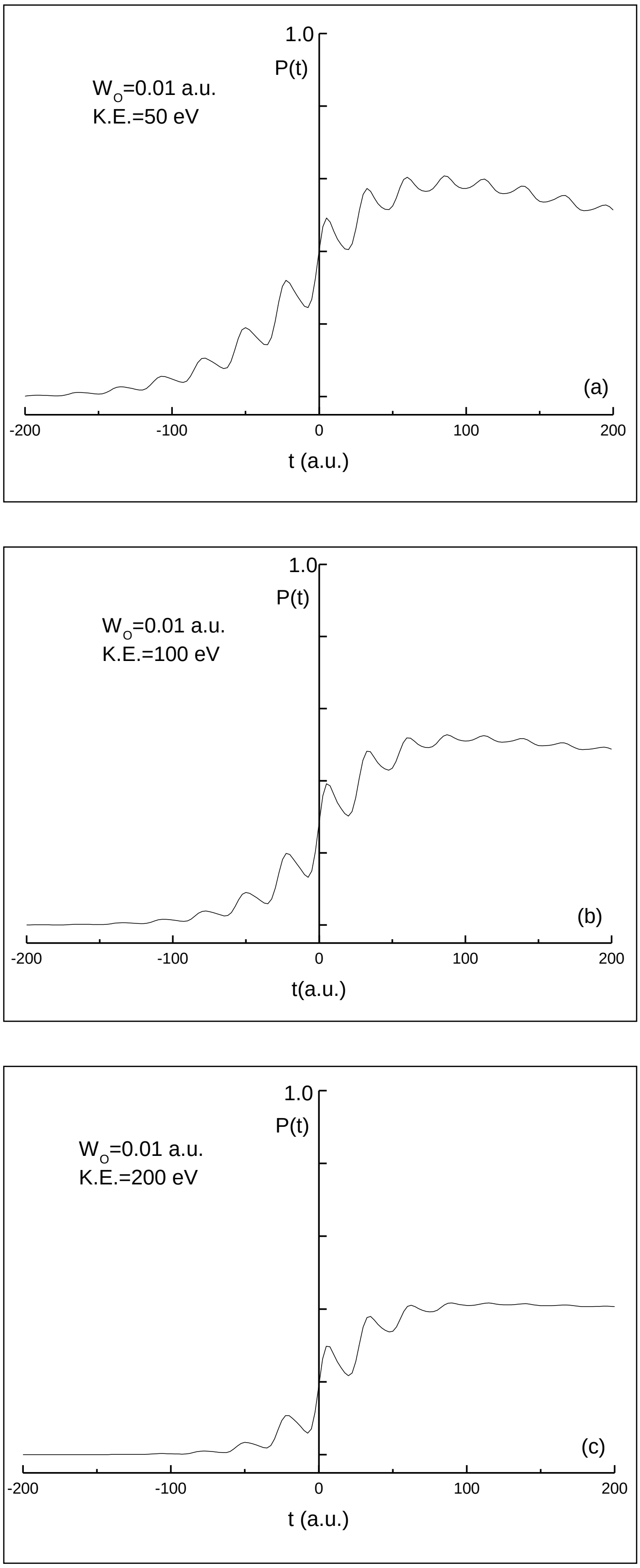


Fig.(5):The neutralization probability of Li^+ as a function of time in the presence of laser field with $W_o = 0.01\,\mathrm{a.u.}$ for three different values of ion kinetic energies.

Since $P(\infty)$ is the main quantity of interest because it is what experimentally measured, the neutralization probabilities are graphed as a function of the incident kinetic energy in fig. (6) with $W_o = 0.01 a.u.$ and $\omega_L = 0.2207$ a.u.. Fig. (7a) shows that far away from the scattering region $P(\infty)$ increases with W_o . While in fig.(7b), the ion neutralization probability variation with laser strength has calculated at ion kinetic energy 100 eV using the same value of laser frequency.

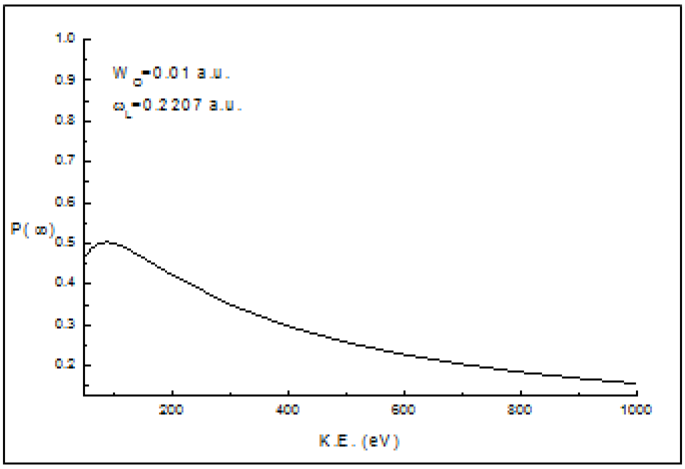
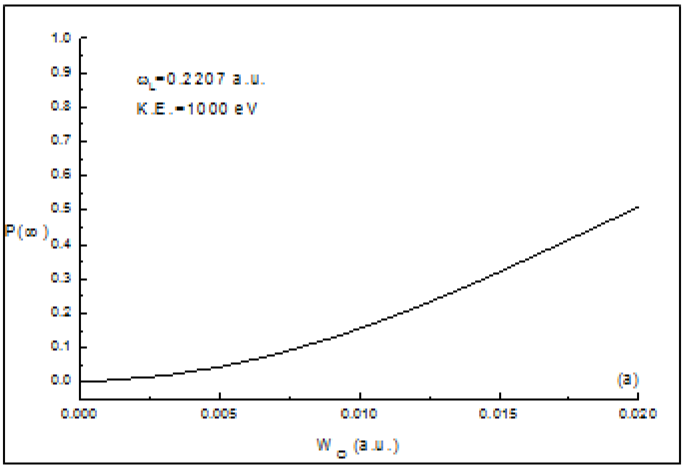
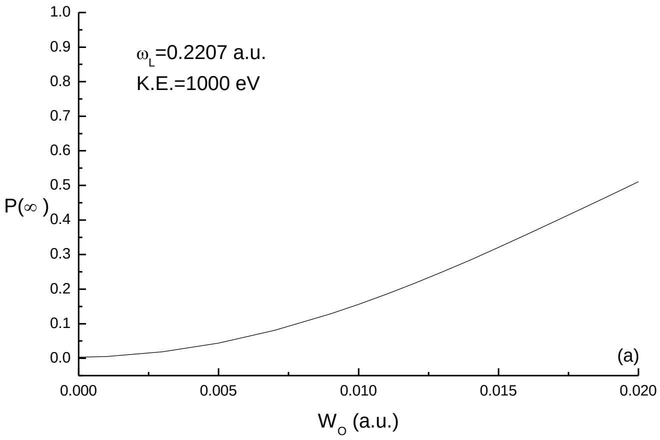


Fig.(6):The neutralization probability variation with ion kinetic energy for $W_o = 0.01$ a.u..





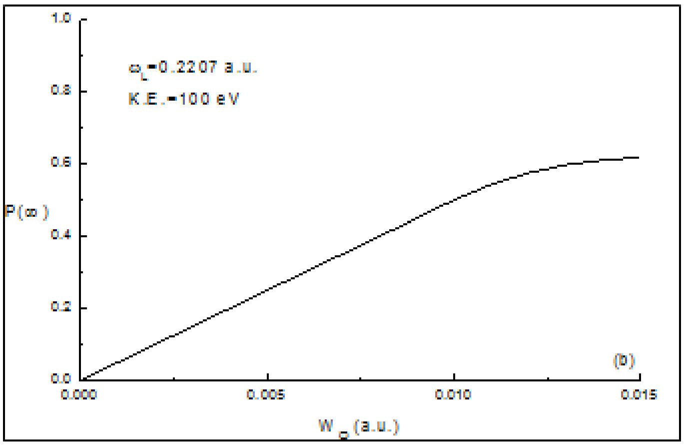
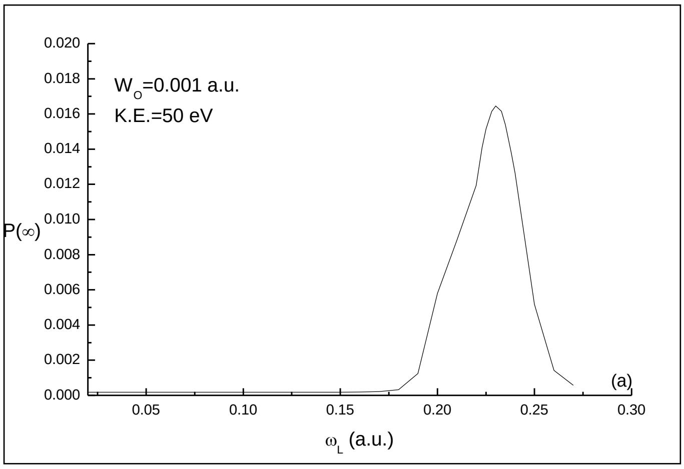


Fig.(7):The neutralization probability variation with the laser coupling for tow different values of ion kinetic energies.

Finally, to know more about laser effect, $P(\infty)$ are calculated as a function of ω_L for three different values of $W_o = 0.001, 0.005, 0.01\,\mathrm{a.u.}$ with ion kinetic energies equal to 50, 100, 200 eV in figs (8),(9) and (10) . Fig. (10a) clarify again our above-mentioned notes about the oscillatory behavior at low ion kinetic energy and the dependence of the peaks positions on the other parameters. The peaks positions, in fig (10a), lie nearly at 0.209a.u. (5.686 eV) and at 0.235a.u. (6.394 eV). The first one makes the atomic energy level matches the upper edge of the band while the second makes it matches the centre of the band where the ion's valance level is interacting with the band energy levels rather than just a single one. So $P(\infty)$ at $\omega_L = 0.235\,\mathrm{a.u.}$ is greater than $P(\infty)$ at $\omega_L = 0.209\,\mathrm{a.u.}$.At higher ion's kinetic energy, the peaks positions in figs (8),(9) and (10) lie at the same value of $\omega_L \approx 0.23\,\mathrm{a.u.}$, but $P(\infty)$ for $W_o = 0.01\mathrm{a.u.}$ is greater than $P(\infty)$ that calculated for $W_o = 0.001, 0.005\,\mathrm{a.u.}$. From this curve one can determine the value of ω_L at which the neutralization probability becomes large keeping in mind that this value depends also on the choice of other parameters.

According to our results, we conclude that the study of laser-assisted surface-ion charge transfer process requires the addition of two terms (denoted in eq.(5)) to the one electron Hamiltonian which describes the coupling between the species and solid surface orbitals due to their interaction with the electromagnetic field of laser.

Our calculations for neutralization probability can be considered as system-characteristic which is very helpful (for the corresponding experiments) in determining the required way of charge transfer, i.e. determining the species final charge state which can be controlled by laser field.



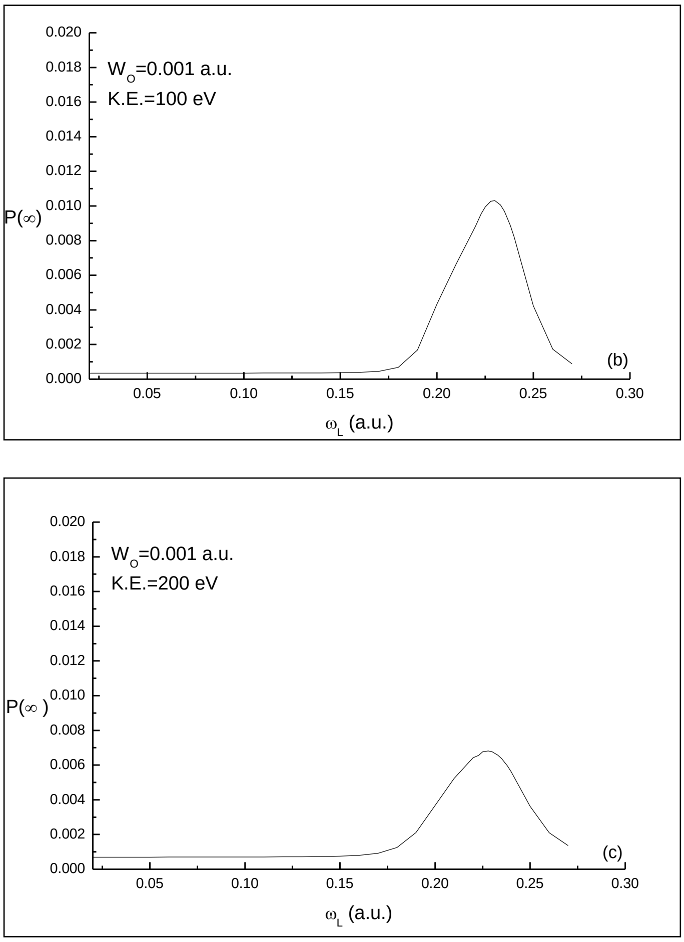
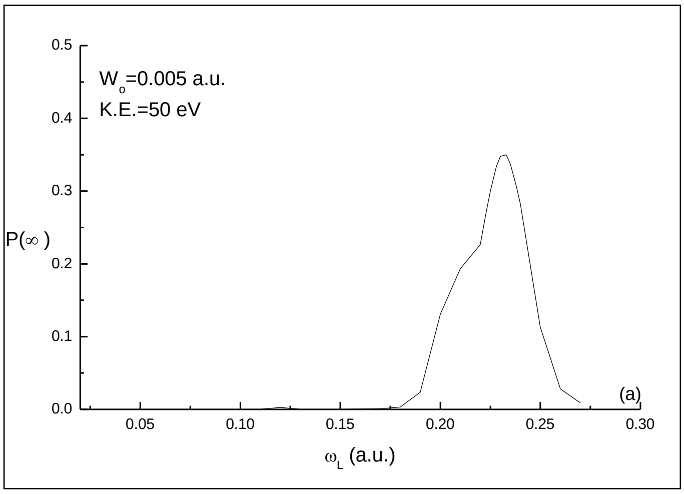
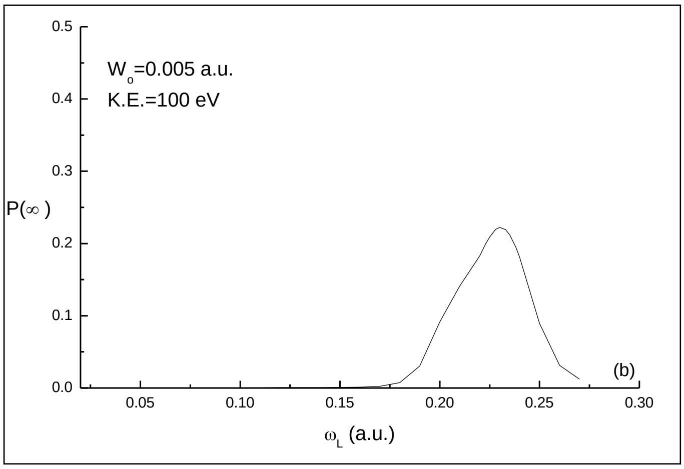


Fig.(8):The Li^{+} neutralization probability as a function of laser frequency with $W_o = 0.001\,\mathrm{a.u.}$ for three different values of ion kinetic energies.





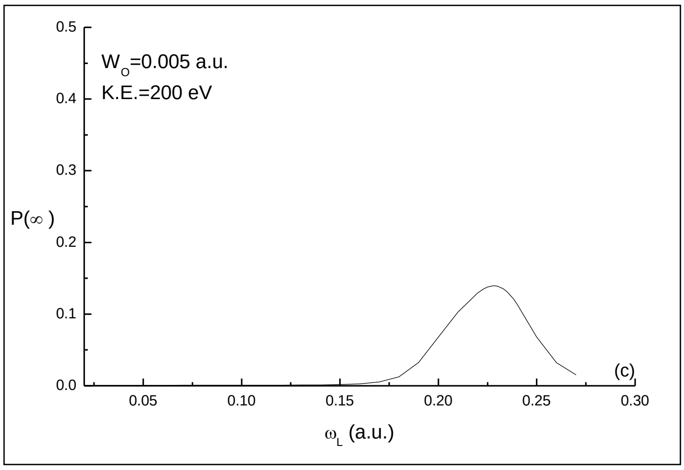
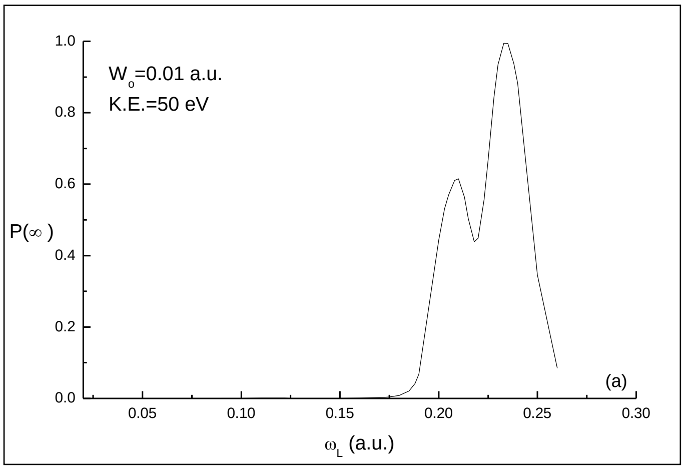


Fig.(9):The Li^{+} neutralization probability as a function of laser frequency with $\mathrm{W_o} = 0.005\ \mathrm{a.u.}$ for three different values of ion kinetic energies.



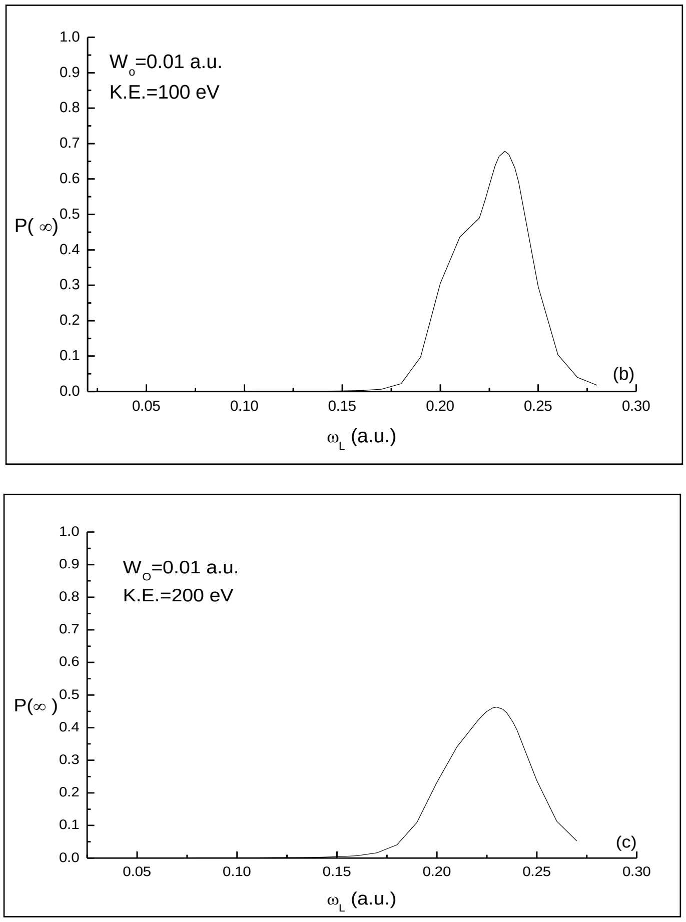


Fig.(10):The Li^{+} neutralization probability as a function of laser frequency with $W_o = 0.01\,\mathrm{a.u.}$ for three different values of ion kinetic energies.

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