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حساب المقطع العرضي للإلكترونات الضوئية لمدارات فرعية لذرة فوسفور في مركباته

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(قبل للنشر في 2002/9/18)

□ الملخّص □

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تعتمد شدة الإلكترونات الضوئية أو المساحة التي تشغلها هذه الخطوط على عدة عوامل منها: المقطع العرضي، عمق الانفلات للإلكترون، نفوذية مقياس الطيف، عدم تجانس الطبقة السطحية للعينة.

لذلك، يهدف هذا العمل إلى حساب المقطع العرضي للإلكترونات الضوئية لمدارات فرعية في ذرة الفوسفور في بعض مركباته.

بعد تحديد المقطع العرضي يمكننا تخمين احتمال إنتاج الكترون ضوئي في مدار فرعي لكل فوتون ساقط على العينة.

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1.Introduction:

Photoelectric cross – section :

The term cross-section is used as a quantitative measure of an interaction between an incident particle and an atom.

The cross-section σ per atom for a given process is defined through the probability, P= number of interactions /number of incident particles.

$$P = Nt\sigma \qquad (1)$$

Where N the number of atoms per unit volume in the target and t is its thickness .

The number of interaction for a target containing Nt atoms per unit area perpendicular to an incident beam of I particles is equal to INtσ .

Another unit of thickness is the mass absorption coefficient (the product of the mass density D_m and the linear thickness t).

In this work we describe a calculation of the photoelectric cross-section using hydrogenic wave functions .

For this calculation we use an equation that is famous in quantum mechanics and is known as Fermi's Golden Rule[1] .

Fermi's Golden Rule provides us the probability per unit time for a transition to the final state f from the initial state i between atom –orbits and is given by ,

$$W = \frac{2\pi}{\hbar} D(E) \left| \langle \psi_f | H' | \psi_i \rangle \right|^2 \qquad (2)$$

Where W is the transition rate and has dimension (time)$^{-1}$.

In this equation D(E) is the density of final states per unit energy.

Here, the three dimensional density of states is given by,

$$D(E) = \left(\frac{V}{2\pi^2} \right) \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} \qquad (3)$$

The most useful formula to calculate the probability of a transition comes from time-dependent perturbation theory.

It's the formula which is the starting point for many of the derivations of cross-sections. Consider system with a Hamiltonian H given by,

$$H = H_o + H' \qquad (4)$$

Where H_o is a time – independent operator and could be ,for example, the Hamiltonian which describes hydrogenic atom while H' may be a time – dependent perturbation.

$$\langle \psi_f | H' | \psi_i \rangle = \int \psi^*_f H' \psi_i \, d\tau = \left| H'_{fi} \right| \qquad (5)$$

Where ψ^* is the complex conjugate of ψ , $d\tau$ is a three dimensional volume element .

X- ray photoelectron spectroscopy (XPS) is an example of a process that involves one atomic transition , the creation of an inner hole and an energetic photoelectron Fig.1.

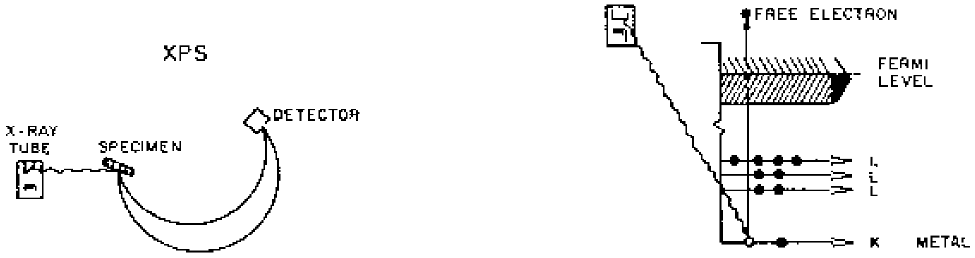

Fig.1:Schematic diagram of X-ray photoelectron spectroscopy

The relevant wave functions for the initial and final states are given by ,

$$\psi_i(r) = \frac{1}{\sqrt{\pi a}} e^{-\rho} \qquad (6)$$

$$\psi_f(r) = \frac{1}{\sqrt{V}} e^{ikr} \qquad (7)$$

where $\rho = r/a$, $a = a_0/Z$, a_0 - Boher –radius ,Z- atomic number.

The initial state ψ_i describes a ground state hydrogenic wave function in an atom and the final state ψ_f is usual outgoing plane wave normalized to a volume V.

In this calculation we assume the energy of the incoming photon $\hbar\omega$ on the target is more bigger than the binding energy E_B of the orbit- electron .

The transition probability can be calculated explicitly if the perturbation potential **is**

$$H'(z,t)=H'(z)e^{-i\omega t}=-ez\mathcal{E}e^{-i\omega t} \qquad (8)$$

Where $\mathcal{E}$ an applied electric field which acts on the particle in z direction.

From eqs.(2-8) we get W. The cross- section σ is defined

as the ratio between W and the flux F of the incident electromagnetic radiation (the number of photons/area/time)[1].

$$\sigma = W/F \qquad (9)$$

The measurements for the binding energy of electrons were performed with XPS- method. By means of XPS-, a bound electron such as the K-shell electron promoted to a free state outside the sample, see Fig.1 .

The kinetic energy of the photoelectron is well defined and sharp electron peaks appear in the spectrum.

In XPS , the sample is irradiated by constant photon energy $\hbar\omega$ and the kinetic energy of the electrons measured by means of spectrometer[2,3,4] .The relevant energy conservation equation is,

$$\hbar\omega + E^i_{tot} = E_{kin} + E^f_{tot}(K) \qquad (10)$$

Where E^i_{tot} is the total energy of the initial state, E_{kin} is the kinetic energy of the photoelectrons , and E^f_{tot} is the total energy of the system after ejection of the photoelectron from the K- level.

The binding energy of the photoelectron is defined as the energy required to remove it to infinity with a zero kinetic energy .

$$\hbar\omega = E_{kin} + E^V_B(k) \qquad (11)$$

Where $E^V_B(K) = (E^f_{tot} - E^i_{tot})$ is the binding energy of an electron in the K-level referenced to the local vacuum level. In the solid state , the Fermi-level is used as a reference niveau . Then ,

$$\hbar\omega = E_{kin} + E^F_B(K) \qquad (12)$$

In this work we consider the case that $\hbar\omega \gg E_B$, so that $E \cong \hbar\omega$.

Under this condition the final results for the photoelectric cross-section σ_{ph} yields,

$$\sigma_{ph} = \frac{7.75}{\hbar\omega}\left(\frac{E_B}{\hbar\omega}\right)^{\frac{5}{2}} \quad Å^2 \qquad (13)$$

From (13) we notice that σ_{ph} decreases with increasing photon energy **as** $(\hbar\omega)^{5/2}$.

Electron Impact Ionization Cross-Section :

The cross-section for an inelastic electron-electron collision σ_e can be derived by using impulse approximation for scattering in central force field. Then, σ_e is given by,

$$\sigma_e = \pi e^4/EE_B \qquad ; E \gg E_B \qquad (14)$$

Where E the energy of the incident electron beam and E_B is the binding energy of orbital –electron .

2. Results

during the XPS measurements the specimens were irradiated with Al $K_\alpha(h\nu) = 1486.6eV$ to obtain P_{2s} , P_{2p} - binding energies.

Table 1 contains 5 samples of phosphorus and P_{2s} , P_{2p} - binding energies in eV[5].

Nr	Sample	$E_B(P_{2s})$	$E_B(P_{2p})$
1	P	188.25	130.65
2	InP	188.5	128.85
3	GaP	187.05	129.4
4	Na_3PO_4	190.15	132.75
5	NH_4PF_6	194.8	137.65

Table 1: contains samples, P_{2s} , P_{2p} –binding energies.
All values are given in eV

The calculation of σ_{ph} of phosphorus-subshells are presented in table 2 according to eq. (13).

In addition , table 2 illustrates ,for comparison, values of σ_e according to eg.(14) with supposing the electron beam energy is the same as the energy of the K_α - photons.

Nr	$\sigma_{ph}(P_{2s})$	$\sigma_{ph}(P_{2p})$	$\sigma_e(P_{2p})$	χ [6]	$\Delta\chi$
1	2.85	1.14	335.19	2.19	0
2	2.79	1.10	340.10	1.78	-0.41
3	2.81	1.12	338.86	1.81	-0.38
4	2.93	1.19	330.10	3.44	1.25
5	3.11	1.30	318.34	3.95	1.76

Table 2 : contains cross-section $\sigma \times 10^{-21} cm^2$, electronegativity χ and electronegativity difference $\Delta\chi$ between P and its adjacent –atoms.
Numbers correspond to compounds listed in table 1

3. Discussion

From table 2 we notice that the shifts of the cross-section between P-compound are small . Thereby , one infers that the environment of phosphorus couldn’t have affects on the σ_{ph} Fig.2 .

As expected, the dependence has weak effects on the cross-section[7].

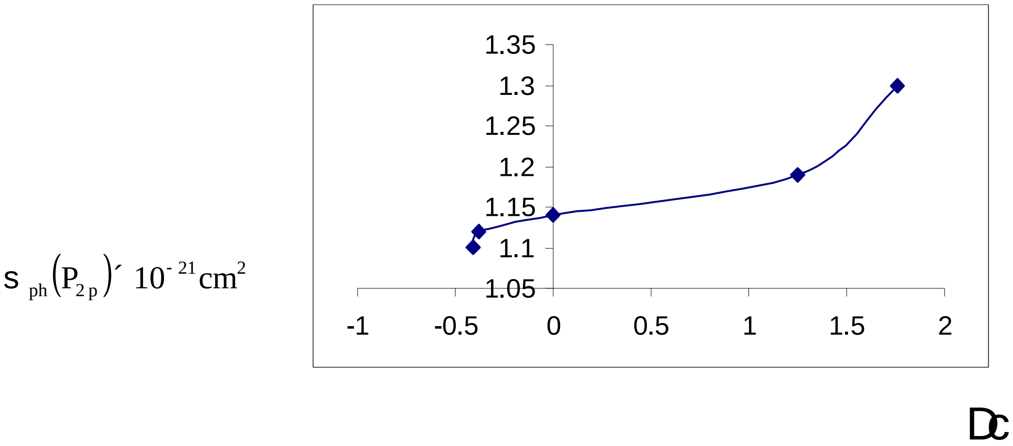

Fig.2. The dependence of σ_{ph} on the difference in Pauling’s electronegativity $\Delta\chi$ between phosphorus and the neighbourig atoms.

From Fig.3 one can see a linear relationship between $\sigma_{ph}(P_{2p})$ and $\sigma_{ph}(P_{2s})$.

This relation reflects a stronger interaction of the 2s-subshell with the incident radiation in contrast to the 2p-subshell.

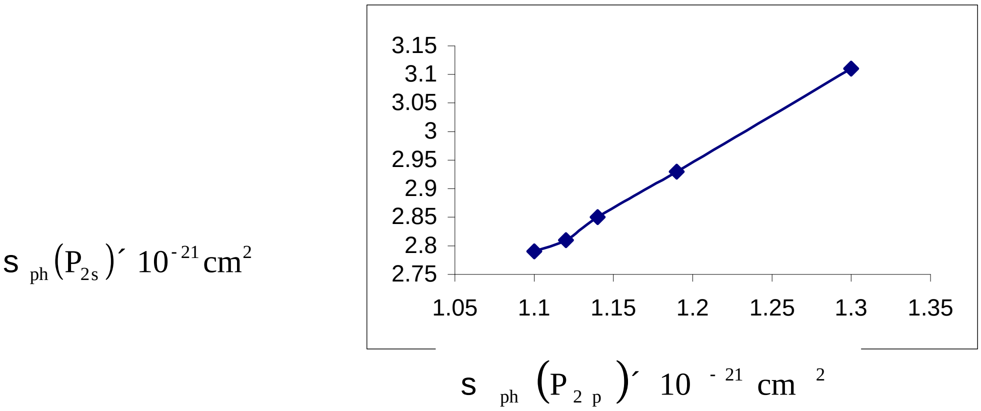

Fig.3: correlation $\sigma_{ph}(P_{2s})$ with $\sigma_{ph}(P_{2p})$

As can be seen from Fig.4 the σ_e values are always larger than the corresponding σ_{ph} values, as electrons are charged particles in comparison with photons.

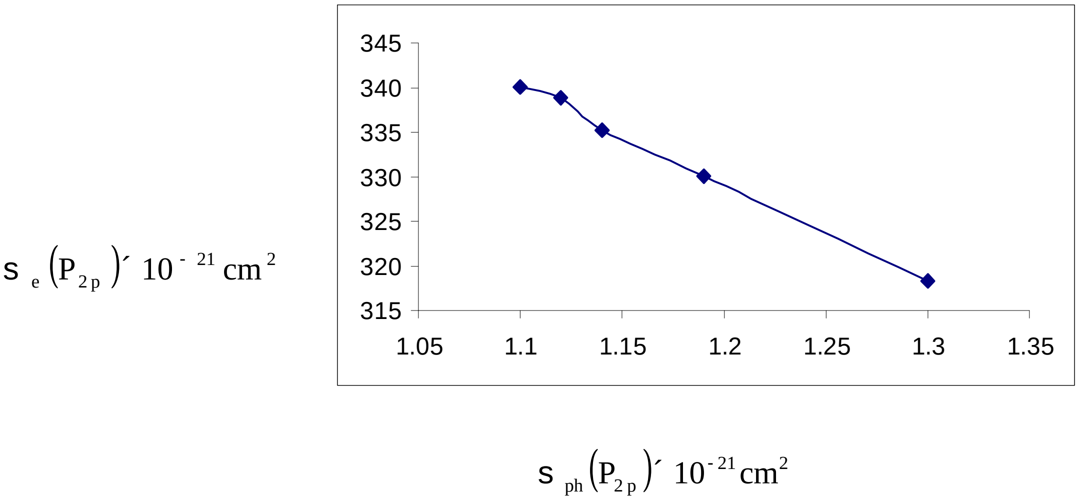

Fig.4: **Comparison of σ_{ph} with σ_e**

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