June 2008 Volume 7 Issue 7

Trade Science Inc.

Analytical CHEMISTRY
An Indian Journal

Full Paper

ACAIJ, 7(7) 2008 [554-557]

Extrinsic and intrinsic plasmon effects in $2P_{½}$ X-ray satellite spectra of titanium and copper compounds

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Received: 18th May, 2008 ; Accepted: 23rd May, 2008

ABSTRACT

An alternative explanation for the high energy X-ray satellites of $2P_{1/2}$ main line of titanium and copper halides is being presented with a new approach by considering both extrinsic and intrinsic contribution simultaneously. The values calculated for energy separation and relative intensity agree better with the experimentally observed values. The importance of plasma oscillation is found in X-ray satellite spectra of titanium and copper halides.

KEYWORDS

X-ray satellite spectra;
Plasmon;
Energy separation;
Relative intensity;
Intrinsic;
Extrinsic effects.

INTRODUCTION

X-ray satellites or non-diagram on high energy side of parent emission lines are well known in X-ray emission spectra. Plasmon theory has been proved very successful in explaining the origin of all those high energy satellites which are found at an energy separation of $\hbar\omega_p$ (plasmon energy) from the main emission X-ray line. This theory has been successfully used in explaining many α, β and γ satellites[1-4]. The involvement of plasma oscillation in X-ray emission spectroscopy (XPS) data have been studied by many authors and their origin has been the source of active debate for a ling time. Among them satellite structure in halides have received much attention[5-11] and have been the subject of controversy for some time. Several workers[4,12] have explained satellite structure in halides using plasma oscillation theory, but discrepancy in results could not be removed successfully. In the present work authors have applied a new approach to explain the discrepancy in the satellite structures of halides using plasmon theory in the new light. The experimental data for titanium compounds were taken form[13-15]. and for copper halides from reference[16]. The collective oscillation experienced by electron density of solid due to certain charge imbalance are called plasma oscillation and quantum of energy of these plasma oscillation is named as plasmon by Bhom and Pine[17-20]. According to K.S.Srivastava et.al.[1] during X-ray photoemission process the transiting valance electron excites a plasmon in valance band. The transition energy of main line is thus shared between plasmon ($\hbar\omega_p$) and the emitted photon of low energy. However, if the plasmon pre-exists, then during X-ray photoemission process it can transfer its energy ($\hbar\omega_p$) to the transiting valance electron before it annihilates the core vacancy. Thus energy of emitted X-ray photon will be higher than the energy of main line by amount ($\hbar\omega_p$). The emission line owing to this process is known as High Energy Satellites and has been observed by large number of workers[21-24]. According to what has been said above, the energy separation (E)

TABLE 1: Energy separation of titanium and copper compounds

Compounds	Z'	σ	W	Calculated energy separation (ev)			Observed energy
				$\hbar\omega_p$	$\hbar\omega_s$	$2\hbar\omega_s$	Separation[13-16] (ev)
$TiCl_4$	6	1.73	189.71		4.76		4.0
						9.5	9.7
TiO_2	8	4.23	79.87		13.3		13.3
CuF_2	3	4.23	101.54		7.2		7.0
$CuCl_2$	3	3.39	134.44	7.9			8.8
$CuBr_2$	3	4.71	223.31			10.0	10.0

of high energy satellites from main emission line should be equal to quantum of plasmon energy (either bulk plasmon, single surface plasmon or double plasmon) which can be calculated by the formula given by Marton et.al[25] as- **Bulk plasmon energy = 28.8 $(Z'\sigma/W)^{1/2}$ (ev)**

Where Z' = effective number of electrons taking place in plasma oscillation, s = specific gravity, W = molecular weight of compounds. And surface plasmon energy using formula given by Ritche[26] as calculated in TABLE 1.

$$\textbf{Surface plasmon energy} = \frac{\hbar\omega_p}{\sqrt{2}} \text{(ev)}$$

This equation is valid for free electron model, but to a fairly good approximation, it can be used for semiconductors and insulators. The present calculated values of surface plasmon energy in TABLE 1 are in better agreement with experimentally observed[13-16] values.

Relative intensity calculation

Hence, from energy considerations alone, the satellite can be regarded as being due to excitation of plasmon, but in order to further confirm the involvement of plasmon authors calculated the relative intensity (I_s/I_m) of these satellites using plasmon theory in new light. There are two types of plasmon excitation-extrinsic and intrinsic[27]. In extrinsic process, excitation of plasmon occurs during transport of electrons through solid (fast electron process); while in intrinsic process excitation of plasmon takes place simultaneously with the creation of hole (slow electron process). According to Bradshaw [28] in intrinsic process slow electrons are not is not conserved; plasmon satellites are strong. Now in the present work author has tried to incorporate both the processes i.e. the relative contribution of extrinsic process in as well as the second intrinsic case in which the number of slow electrons is conserved. The authors have gone through detailed survey of the literature regarding this and found that Pardee et.al.[29] have done the remarkable job in combining both extrinsic and intrinsic effects[27] in one equation simultaneously with some inelastic effects and have given formula for the combined relative intensity as-

$$i = \alpha_n \sum_{m=0}^{n} \frac{(\beta/\alpha)^m}{m!} \qquad (1)$$

Where $\alpha = (1+1/L)^{-1}$ (2)

is inelastic loss factor, which gives the relative intensity for extrinsic satellites. Here l = mean free path for extrinsic plasmon excitation, L = mean attenuation length for electrons due to processes other than plasmon excitation.

The parameter β is a measure for the probability P_i (n) for intrinsic excitation of n plasmons-

$$Pi\,(n) = e^{-\beta}\,\frac{\beta^n}{n!} \qquad (3)$$

The value of β[30-33] is taken as $\beta = 0.12 r_s$ (4)

which has been used for intrinsic relative intensity by K.S.Srivastava et.al.[4] and clearly an approximation and one term of (1).

But in the present case Pardee's equation (1) directly with the same values of α and β given by equations (2) and (3) respectively could not be used because it does not give satisfactory results, so it need some modification.

Therefore in the way of modification we for the first time, modified α. We have replaced α from inelastic loss factor to the ratio of cut- of wave vector K_c to the Fermi wave vector

as $\alpha = K_c/K_F$ and its value is taken[34] as- $\alpha = 0.47\, r_s^{1/2}$ (5)

Here r_s is dimensionless parameter and is same as used in equation (4); given by[33] as-

$$r_s = (47.11/\hbar\omega_p)^{2/3} \qquad (6)$$

For volume plasmon and for surface plasmon

$$r_s = (47.11/\hbar\omega_p)^{2/3} \qquad (7)$$

Using this new value of α (eqn.-5) along with β

TABLE 2: Relative intensity of titanium and copper compounds

Compounds	r_s	α	Calculated relative Intensity (I_s/I_m)				Observed
			β $\beta^2/2\alpha$	$\beta^2/2\alpha+\beta^3/6\alpha^2$	$\beta+\beta^2/2\alpha+\beta^3/6\alpha^2$	β-0.1	Relative intensity[13-16]
$TiCl_4$	4.6	1.01	0.15				0.12^a
				0.18			0.28
						0.45	0.41^b
TiO_2	2.33	0.72			0.34		0.40
CuF_2	3.5	0.88			0.54		0.80
$CuCl_2$	3.3	0.85			0.49		0.60
$CuBr_2$	4.39	0.99	0.50				0.50

a- experimental results form solid state measurement[13], b- experimental results form gas phase measurement[14

(eqn.-4) in equation, we have calculted a number of excellent results[35-39].

The equation (1) contains a series of terms, which include both extrinsic and intrinsic contributions along with their relative coupling terms. The first term is purely extrinsic, while second term is purely intrinsic. The other terms are containing the relative contributions of both extrinsic and intrinsic. The specialty of this formula is that each term alone or simultaneously[39] with other terms is able to give the relative intensity. It is the type o\f excitation, which decides which and how many terms will be used. This formula also includes both the categories mentioned by Bradshaw and gives better results as compared to that and than traditional methods for calculation of the relative intensity. Using equations (1), (3), (4) and (5) the calculated values of relative intensity are given in TABLE 2 simultaneously with experimentally observed values. Earlier workers[1-4,12] have used various terms of this formal alone to explain successfully the relative intensity of many satellites up to certain extent. But, using various terms of this formula we are able to calculate not only the relative intensity of existing satellites but also it is possible to predict those satellites which are yet to be discovered. It is also the beauty of the method that the relative intensity of higher order satellites can easily be calculated without going in much mathematical details. It is also possible to separate the relative contributions of extrinsic and intrinsic excitations in total intensity. No method is present in the literature which proves the strength of much higher satellites and separates these contributions with such accuracy.

CONCLUSION

Authors calculated values of plasmon energies are in better agreement with the experimentally observed values of energy separation. Now for the calculation of relative intensity compounds are treated microscopically[41]. When treated in this way, the satellites of different compounds slightly differ in assignment from one another in natural way as types of halides differ. But for the similar type of halides the contributions of extrinsic and intrinsic plasmon coupling processes are the same. There is only difference between CuF_2 and $CuCl_2$ in showing low intensity. This might be due to any other reason. So, it can be established beyond doubt that the satellites of $2p_{1/2}$ main line in titanium and copper compounds are due to plasmon gain processes and the consideration of relative contributions of both extrinsic and intrinsic plays an important role in the calculation of relative strength of satellites.

ACKNOWLEDGMENTS

Thanks are due to Prof. K.S.Srivastava (Physics Department, Lucknow University, Lucknow U.P.) and Dr.A.K.Srivastava (Physics Department, Kamla Nehru Institute of Physical and Social Sciences, Sulatnpur, U.P.) for his constant advice and many valuable suggestions.

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