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SURFACE PLASMON SATELLITES IN CORE-LEVEL X-RAY PHOTOEMISSION SPECTRA OF LATE TRANSITION-METAL COMPOUNDS

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The origin of satellites in 2p core level of late transition metal compounds are studied using plasmon theory. The calculated values of energy separation and relative intensity agree well with the experimental values and the theoretical calculations by Kozo Okada et al. The excitation of surface plasmons in 2p core level X-ray photoemission spectra of transition metal dihalides is discussed.

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1. Introduction

X-ray photoemission spectra of core levels in many transition metal compounds show intense satellites occurring on high binding-energy side of the main line [1−5]. Such satellites have been observed in gas phase molecules as well as in solids. Although many models attempting to explain origin of the core-level satellites in halides [6−10] have appeared in the literature, yet at the first sight it appears that these satellites may be due to plasmon excitation processes because their energy separations are in the range of plasmon excitation, and plasmon theory is supposed to be the most suitable theory in this energy range. The existence of bulk and sur-

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face plasmon in X-ray satellite spectra are well known since the theoretical work of Pines and Bohm [11–13]. Pines [14] defined plasmons as quanta of energy of these collective oscillations. In X-ray photoemission spectra, a valence electron, while filling core vacancy, excites a plasmon, then transition energy is shared between plasmon and photoelectron. This process gives rise to low-energy X-ray satellites that have been observed by a large number of workers experimentally and considered theoretically [15–16]. However, if a plasmon pre-exists, then during the X-ray emission process it transfers its energy to the transiting valance electron before it annihilates the core vacancy. Thus the energy of emitted X-ray photon will be higher than the energy of the main line. This process gives rise to high-energy satellites. Although, the excitation of surface plasmon is well known in oxides [17–18] of various metals and compounds, yet the literature is silent about the excitation of surface plasmons even in halides. Since halogens are very near to oxygen in the periodic table and more electronegative than oxygen, the possibility of surface plasmon excitation in halogens can not be ignored. Therefore, we have, for the first time, tried to examine the excitation of surface plasmons [19] in the satellite spectra of transition metal halides.

2. *Energy separation*

Experimental data were taken from published literature from Refs. [20–22]. Although the origin of satellite transition metal halides may also be analyzed by applying different analytical techniques [23], we have applied plasmon theory. In this we applied some modified terms which proved superiority over old plasmon methods [24–27]. We calculated energy separation from the main line using the following formula given by Marton [28]

$$\text{Bulk plasmon energy, } \hbar\omega_p = 28.8\left(Z'\sigma/W\right)^{1/2} \tag{1}$$

where Z' is the effective number of electrons taking part in plasma oscillation, σ the specific gravity and W the molecular weight of compound. Since at the surface more localized oscillations can occur with frequency ω_s, depending on the conditions and the energy of the corresponding peak, surface plasmon may also be seen. Hence we also calculated surface plasmon energies using formula given by Ritchie [29],

$$\text{Surface plasmon energy,} \hbar\omega_s = \hbar\omega_p/\sqrt{2} \tag{2}$$

This equation is valid for free-electron model to a fairly good approximation. It can also be used for semiconductors and insulators. The present calculated values of surface plasmon energy in Table 1 are in close agreement with experimental [20–22] and previously calculated [23] values.

TABLE 1. Values of surface plasmon energy.

Compound	Z'	σ	W	Energy separation (eV)		
				Present work ($\hbar\omega_s$)	Experimental Ref. [20−22]	Calculated Ref. [43]
NiF_2	2	4.72	96.71	6.4	6.0	6.0
CoF_2	2	4.46	96.93	6.3	6.0	6.0
FeF_2	2	4.09	93.84	6.0	6.5	6.4
MnF_2	2	3.98	92.93	6.0	7.0	7.1
$FeCl_2$	3	3.16	126.75	5.6	5.5	5.7
$MnCl_2$	3	2.977	125.84	5.4	5.0	5.6
$FeBr_2$	3	4.636	215.67	5.2	6.0	5.6
$MnBr_2$	3	4.39	214.76	5.04	5.5	5.7

3. Relative intensities

From the energy considerations alone, the satellite can be regarded as being due to an excitation of surface plasmon. But for a further confirmation of involvement of surface plasmon in satellites of these compounds, the relative intensity (I_s/I_m) has also been calculated using plasmon theory in new light. There are two types of plasmon excitation − extrinsic and intrinsic [30]. In the extrinsic process, excitation of plasmon occurs during the transport of electrons through solid (fast electron process), while the in intrinsic process, excitation of plasmon takes place simultaneously with the creation of a hole [31] (slow electron process). In the present work, we have tried to incorporate both these processes, i.e., the relative contribution of the extrinsic process as well as of the intrinsic process in which the number of slow electrons is conserved. We have gone through detailed survey of the literature regarding this and found that Pardee et al. [32] have done the remarkable job in combining both extrinsic and intrinsic effects in one equation simultaneously with some inelastic effects and have given the formula for the combined relative intensity as

$$i = \alpha^n \sum_{m=0}^{n} \frac{(\beta/\alpha)^m}{m!}, \tag{3}$$

where

$$\alpha = \frac{1}{1 + l/L} \tag{4}$$

is the inelastic loss factor, which gives the relative intensity for extrinsic satellites. Here l is the mean-free path for extrinsic plasmon excitation and L the 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 the intrinsic excitation of n plasmons,

$$P_i(n) = \mathrm{e}^{-\beta} \, \frac{\beta^n}{n!} \tag{5}$$

The value of β [33 – 36] is taken as

$$\beta = 0.12 \, r_s \,, \tag{6}$$

which has been used for intrinsic relative intensity by K. S. Srivastava et al. [17] and clearly is an approximation and one term of Eq. (3).

But in the present case, Pardee's Eq. (3) with the same values of α and β given by Eqs. (4) and (5), respectively, could not be used directly because it does not give satisfactory results, so it needed some modifications.

Therefore we modified α. We have replaced α from inelastic loss factor to the ratio of cut-off wave vector K_c to the Fermi wave vector as $\alpha = K_c/K_F$ and its value is taken [37] as

$$\alpha = 0.47 \, r_s^{1/2} \,. \tag{7}$$

Here r_s is a dimensionless parameter and is the same as used in Eq. (6), given by [13]

$$r_s = \left(\frac{47.11}{\hbar\omega_p} \right)^{2/3} \tag{8}$$

for volume plasmon, and for surface plasmon

$$r_s = \left(\frac{47.11}{\hbar\omega_s} \right)^{2/3} . \tag{9}$$

Using the new values of α, Eqn. (7), and β, Eqn. (6), in Eqn. (3), we have calculated several excellent results [38 – 41].

The beauty of Eqn. (3) is that it 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 the second term is purely intrinsic. The other terms give both extrinsic and intrinsic relative contributions. The speciality of this formula is that each term alone or simultaneously [42] with other terms is able to give the relative intensity. It is the type of excitation which decides which and how many terms will be used. This formula also includes both categories mentioned by Bradshaw [31] for intrinsic contributions and gives better results as compared to that and than traditional methods for the calculation of the relative intensity. Using Eqs. (3), (5), (6) and (7), we calculated the values of relative intensity that are given in Table 2, including the experimentally observed values. Earlier workers [17 − 18, 24 − 27] used different terms of this form alone to explain successfully the relative intensities of many satellites up to certain extent. But using various terms of this formula or their combination, we are able to calculate not only the relative intensity of existing satellites, but it is also 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 into much mathematical detail. One can also separate the relative contributions of extrinsic and intrinsic excitations in total intensity. No method is known in the literature which gives the intensities of much higher satellites and separates these contributions with such an accuracy.

TABLE 2. Relative intensities.

Comp.	r_s	α	Intensity assign.	Relative intensity			
				This work	Exptl. Ref. [20-22]	Calc. Ref. [43]	Exptl. Ref. [43]
NiF_2	3.8	0.92	$\beta + \beta^2/(2\alpha)$	0.55	0.60	0.60	
CoF_2	3.83	0.92	$\beta - 0.1$	0.36	0.40	0.40	0.18
FeF_2	3.94	0.93	$\beta^2/(2\alpha)$	0.1	0.20	0.26	0.10
MnF_2	3.97	0.94	$\beta^2/(2\alpha)$	0.11	0.10	0.15	0.06
$FeCl_2$	4.15	0.96	$\beta + \beta^2/(2\alpha)$	0.62	0.65	0.64	
$MnCl_2$	4.22	0.97	$\beta - 0.1$	0.41	0.35	0.35	
$FeBr_2$	4.36	0.98	$\beta + \beta^2/(2\alpha)$	0.66	0.85	0.79	
$MnBr_2$	4.45	0.99	$\beta - 0.1$	0.43	0.45	0.47	0.38

4. *Conclusion*

Authors calculated the values of surface plasmon energies which are in close agreement with the experimentally observed values of energy separation. For the calculation of relative intensity, compounds are treated microscopically [45]. 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. The calculated values of relative intensity are in close agreement with the observed values [20 − 22, 46] and calculated values [23]. So it can be concluded that the core-level satellites of late transition metal dihalides may be due to surface plasmon excitation.

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POVRŠINSKI PLAZMONSKI SATELITI U SPEKTRIMA FOTOEMISIJE IZ SREDICA U SPOJEVIMA KASNIH PRIJELAZNIH METALA

Proučavamo nastanak satelita 2p sredice spojeva kasnih prijelaznih metala primjenom plazmonske teorije. Izračunate vrijednosti pomaka energije i relativnih intenziteta u dobrom su skladu s eksperimentalnima i s teorijskim vrijednostima Kozo Okade i sur. Raspravljamo uzbudu površinskih plazmona rentgenskim zračenjem u fotoemisijskim spektrima 2p sredice dihalida prijelaznih metala.