

LETTERS TO THE EDITOR

LOW ENERGY PLASMON SATELLITES IN
 $K_{\beta_{1,3}}$ X-RAY EMISSION SPECTRA OF
 ^{23}V , ^{26}Fe AND ^{28}Ni

THE energy separations and the relative intensities of the low energy satellites, observed by Salem *et al.* [*Phys. Rev. A-13* (1976) 330] in $K_{\beta_{1,3}}$ X-ray emission spectra of ^{23}V , ^{26}Fe and ^{28}Ni , have been compared with characteristic electron energy losses (*i.e.*, plasmon

have measured the relative intensities and have suggested the origin of the lines to be due to the exchange interaction between the 3 *d* and 3 *p* electrons. Their calculated relative intensities, based on Tsutsumi's Molecular orbital (MO) theory, are much greater than the observed values in each case (see Table I). Therefore, it is thought of great interest to find the other possible cause of the appearance of the satellites.

TABLE I

Elements	Constants	Energy Separation in eV			Relative intensity		
		M.O. Theory ¹²	Observed ¹²	$\hbar\omega_p$	M.O. Theory ¹²	Observed ¹²	Author's Value
^{23}V	$r_s = 2.4$ $\alpha = 0.4$ $\beta = 1.26$	9.07	10.24 ± 1.09	12.5	0.60	0.163 ± 0.016	0.123
^{26}Fe	$r_s = 2.81$ $\alpha = 0.47$ $\beta = 1.36$	13.84	11.71 ± 1.2	10.0	0.66	0.344 ± 0.034	0.203
^{28}Ni	$r_s = 2.289$ $\alpha = 0.38$ $\beta = 1.23$	9.22	12.98 ± 1.9	13.6	0.50	0.112 ± 0.02	0.106

energies) and the relative intensities calculated by the author on the basis of Bohm and Pines' Plasma oscillation theory.

Satellites are the weak lines associated with the main peak in X-ray emission spectra. These non-diagram lines and the theories for its origin have been reviewed by Doodhar¹ and Edwards² respectively. Just after the prediction^{3,4} of plasmon creation in X-ray transitions, Rooke⁵, Arakawa and Williams⁶ confirmed the existence of low energy plasmon satellites (LEPS) in light elements (Li, Be, Na, Mg, Al). In the mean time, Brouers⁷, Glick and Longe⁸ worked out the theories of LEPS. The author has also shown the possibility of plasmon involvement in low energy satellites of manganese⁹, manganese oxides¹⁰ and chromium¹¹. Recently Salem *et al.*¹² have observed non-diagram lines on low frequency side in $K_{\beta_{1,3}}$ X-ray emission spectra of vanadium (^{23}V), iron (^{26}Fe) and nickel (^{28}Ni) at energy separations 10.24 ± 1.09 eV, 11.71 ± 1.2 eV and 12.98 ± 1.9 eV respectively. They¹²

The energy separations of ^{23}V , ^{26}Fe and ^{28}Ni satellites, observed by Salem *et al.*¹², correspond well with characteristic electron energy losses¹³ 12.5 eV, 10 eV, and 13.6 eV respectively. These losses are said to be the experimental plasmon energies^{13,14}. However, 10 eV loss in Fe can be compared with 11 eV which is the calculated plasmon energy¹⁵ of ^{26}Fe . 12.5 eV and 13.6 eV losses in ^{23}V and ^{28}Ni agree well with the theoretical plasmon energies 13.98 eV and 11.2 eV respectively. The theoretical plasmon energies in ^{23}V and ^{28}Ni can be obtained from the relation¹⁶ $\hbar\omega_p = 28.8 (Z\sigma/W)^{1/2}$ eV, where *Z* represents valence electrons ($Z_{\text{V}}^{17} = 2$, $Z_{\text{Ni}}^{17} = 1$) in metals, σ is sp. gravity ($\sigma_{\text{V}} = 6.00$, $\sigma_{\text{Ni}} = 8.902$) and 'W' indicates atomic wt. of the elements ($W_{\text{V}} = 50.94$ and $W_{\text{Ni}} = 58.71$). Therefore the satellites in $K_{\beta_{1,3}}$ X-ray emission spectra of ^{23}V , ^{26}Fe and ^{28}Ni may be due to plasmon excitations.

In order to confirm the above statement, we have further calculated the relative intensities. Srivastava,

Singh and Shrivastava¹⁸ have derived the relative intensity expression as—

$$i = a \left[1 - \frac{3}{2} \left(\frac{2}{\beta} \right)^{1/2} \tan^{-1} \left(\frac{\beta}{2} \right)^{1/2} + \frac{1}{2} \frac{1}{(1 - \beta/2)} \right] \quad (1)$$

where α and β ¹⁹ can be given by $r_s/6$ and $0.814\sqrt{r_s}$, respectively. The interelectronic spacing (r_s) in Bohr radius is determined from plasmon energy. The relative intensities of LEPS of ²³V, ²⁶Fe and ²⁸Ni, according to equation (1), have been calculated and found to be 0.123, 0.203 and 0.106 respectively. These values agree fairly well with those observed by Salem *et al.* (see Table I).

On these grounds, the low energy satellites in $K_{\beta_{1,2,3}}$ X-ray emission spectra of ²³V, ²⁶Fe and ²⁸Ni at energy separations 10.24 ± 1.09 eV, 11.71 ± 1.2 eV and 12.98 ± 1.9 eV respectively are LEPS.

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PREPARATION OF DIETHANOLAMINEMANGANATE(III)

REPORTS on metal complexes containing manganese in the tervalent state are very few¹⁻⁵. Maria and Loana⁶ and Edward *et al.*⁷ reported the formation of the manganese(II)diethanolamine complex. Recently Okimoto *et al.*⁸ reported that manganese(III)triethylene-tetramine complex is a powerful initiator of vinyl polymerization. We present here the preparation for the first time of Bisdiethanolaminemanganate(III).

Manganese(II)sulphate monohydrate (0.05 mole) was dissolved in approximately 600 ml of water. Sodium hydroxide (0.10 mole) was added and the precipitate was allowed to settle. The pH of the solution was raised to 9.5 by the addition of 1 ml of 0.01 M sodium hydroxide solution. Oxygen was bubbled through this solution for 1 hour to effect a rapid quantitative conversion of Mn(OH)₂ to Mn(OH)₃. The precipitate of Mn(OH)₃ was filtered transferred to a beaker, 0.10 mole of diethanolamine was added along with 20 ml of ethanol and the mixture stirred well for 1 hour. A red slurry was formed which after washing with ethanol, ether and drying *in vacuo* yielded reddish brown solid. The complex was insoluble in common organic solvents.

Anal : Calc. : Mn, 20.98 ; N, 10.69 ; C, 36.64 ;
H, 6.87.

Found : Mn, 20.88 ; N, 10.62 ; C, 36.43 ;
H, 6.83.

The electronic spectra of the complex in sulphuric acid solution, exhibits a single band at 20,000 cm⁻¹ which can be attributed⁹ to the ⁵T_{2g} ← ⁵E_g absorption expected in an octahedral symmetry. The absence of a band at 3200 cm⁻¹ and above, in the infrared spectra, indicates the absence of any coordinated water or hydroxyl group. The shift of ν(NH) frequency to lower wave number, *viz.*, 3025 cm⁻¹ in comparison to the free ligand¹⁰ (3140 cm⁻¹) indicates the coordination of the diethanolamine through the nitrogen atom.

The thermal decomposition of the solid complex was examined from 70° to 700° C by using a thermo-balance (Perkin Elmer Model TGS-2). The absence of water of crystallisation or loosely bound water was confirmed by the absence of weight loss at about 100° C. The weight loss at about 420°-460° C may correspond to the decomposition of the diethanolamine part and