

Bonding Effect on F $K\alpha$ Satellite Structure Produced by 84-MeV N^{4+}

M. Uda, H. Endo, K. Maeda, Y. Awaya, M. Kobayashi, Y. Sasa, H. Kumagai, and T. Tonuma

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

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The intensity distributions of F $K\alpha$ satellites produced by 84-MeV N^{4+} bombardment displayed a significant chemical effect. The dependence of the intensity distributions of several fluorides on the chemical environment is discussed in relation to the Pauling bond ionicity or covalency. A refilling of vacancies by ligand valence electrons prior to the x-ray emission accounted for the observed satellite distributions for the compounds used.

The use of enhanced $K\alpha$ satellites produced by heavy-ion impact has received much attention in recent years. Several investigations of change in intensity distributions of satellites have been performed on chemical compounds of F, Al, Si, S, and Cl.¹⁻⁵ To explain chemical effects, an L -shell vacancy refilling process through an interatomic transition has been postulated but the argument is still a matter of conjecture.

In the present Letter we report on measurements of the F $K\alpha$ x-ray satellites produced by 84-MeV N^{4+} impact on a series of fluorides, where intensity distributions vary to a large extent from one compound to another. With use of the observed relative intensities, an L -shell vacancy rearrangement probability and an L -shell width for a multiply ionized state were determined quantitatively for the first time. We found that the interatomic transition takes place only through a covalent component in the molecular orbital in the fluorides.

N^{4+} beams were accelerated by the cyclotron of the Institute of Physical and Chemical Research. An on-line Bragg spectrometer was equipped with a rubidium acid phthalate (010) flat crystal and employed a flow-mode proportional counter operated at 1 atm of P -10 and biased to 1900 V as the detecting element. Data were accumulated for fixed periods of charge integration. Evaporated thin films of NaF, Na_3AlF_6 , AlF_3 , NiF_2 , and CuF_2 on Al backing ($2\ \mu\text{m}$ in thickness), and a sheet of Teflon, $(CF_2)_n$, without backing, all in 1-2-mg/cm² thickness which caused ~ 4 -MeV energy loss of the beams, were used.

No enhancement of the F $K\alpha$ diagram line was observed even when the NaF target backed with thick Al foil, the Al backing being faced on downstream of the incident ions, or coated with Al layer on its surface, the Al layer being faced on upstream, was bombarded with N^{4+} . The spectra obtained in this experiment are then composed

only of ion-induced x rays and free from F K x rays induced by secondary x rays and electrons. No correction was made for differences in self-absorption in the energy range from F K^1L^0 to K^1L^2 lines because energies of the absorption edge of F, for example, in NaF [~ 689 eV (Ref. 6)] and in AlF_3 [~ 692 eV (Ref. 6)] are higher than that of the F K^1L^2 line, where K^1L^n denotes a configuration with a single K vacancy and n L vacancies. Higher-order peaks than K^1L^2 were omitted from the evaluation of peak intensities, because their intensities even if modified by an absorption correction were estimated to be less than 5% of the total intensity. All the spectra were analyzed in terms of a least-squares peak-fitting procedure employing Gaussian functions. The observed relative intensities y_n^X of the F $K\alpha$ spectra are listed in Table I. No distinct chemical shift of the satellite lines could be observed. The difference in the chemical character of these fluorides is, however, strongly reflected in spectral shapes, as shown in Fig. 1. Such a systematic change in intensity distributions relates to the Pauling bond ionicity or covalency.⁷

The F L shell forms a part of the valence band of the fluoride. The plasmon lifetime in solids⁹ is, in general, much shorter than the single- K -vacancy radiative lifetime of the F atom⁸ (2.4×10^{-13} sec). Prior to the F K -x-ray emission, the vacancies of the L shell produced by ion impact can then be transferred to the valence bands of neighboring atoms through molecular orbitals. Let us assume the vacancies in the F L shell to be filled, one by one, by the ligand valence electrons and also assume a probability of simultaneous multielectron transfer to be negligibly small. Then the probability for an L -shell-vacancy rearrangement by one electron $f_{n,n-1}$ is expressed as $\Gamma_L(K^1L^n)/[\Gamma_K(K^1L^n) + \Gamma_L(K^1L^n)]$ for a $K^1L^n \rightarrow K^1L^{n-1}$ transition where $\Gamma_L(K^1L^n)$ and $\Gamma_K(K^1L^n)$ denote L - and K -shell widths for a vacancy con-

TABLE I. Pauling bond ionicity, relative $K\alpha$ x-ray satellite intensities y_n^x , L -shell refilling probability f , ratio of the fluorescence yield ω_2/ω_0 , and L -shell width Γ_L for several fluorides.

Compound	Ionicity ^a	y_n^x ^b			f	ω_2/ω_0	Γ_L ^d ($10^{-4}/\text{a.u.}$)
		$n=0$	$n=1$	$n=2$			
NaF	0.91	0.382	0.412	0.206	-0.032 ± 0.03	1.222 ^c	-2.3 ± 2.0
Na ₃ AlF ₆	0.86	0.421	0.348	0.231	0.138 ± 0.010	1.68 ± 0.10	11.8 ± 1.2
AlF ₃	0.79	0.466	0.306	0.228	0.267 ± 0.013	1.93 ± 0.10	26.9 ± 0.9
NiF ₂	0.70	0.516	0.292	0.192	0.343 ± 0.017	1.73 ± 0.12	38.5 ± 1.2
CuF ₂	0.66	0.531	0.278	0.191	0.381 ± 0.019	1.82 ± 0.12	45.4 ± 1.5
(CF ₂) _n	0.43	0.574	0.242	0.183	0.477 ± 0.043	2.05 ± 0.21	67.3 ± 3.0

^aThe ionicity I is defined by Pauling to be $I = 1.0 - \exp[-0.25(x_A - x_B)^2]$ with x_N the electronegativity of element N (Ref. 7).

^bThe sum of the statistical errors for the intensities and those induced by the deconvolutions was at most 10% and typically much smaller.

^c ω_2/ω_0 of Ne is used only for NaF.

^d Γ_L is estimated using the theoretical value of $\Gamma_K(K^1L^0) = 73.8 \times 10^{-4}/\text{a.u.}$ (Ref. 8).

figuration state of K^1L^n . Then the relative intensity of n^{th} satellite line y_n^x is expressed, through a cascading process,¹⁰ as

$$y_n^x = (\omega_n/\tilde{\omega})(1 - f_{n,n-1})(y_n + f_{n+1,n}y_{n+1} + f_{n+2,n+1}f_{n+1,n}y_{n+2} + \dots + f_{8,7}f_{7,6} \dots f_{n+1,n}y_8), \quad (1)$$

where y_n , ω_n , and $\tilde{\omega}$ are a primary vacancy distribution and a fluorescence yield for K^1L^n , and an average fluorescence yield, respectively. Here the number of L -shell electrons in bonded F^- is to be 8 and $f_{n,n-1} = 0$ for $n=0$. The difference in the chemical environment of F^- must then be reflected in the observed intensity distributions through $f_{n,n-1}$ and $\omega_n/\tilde{\omega}$. For small n we assume that $\Gamma_K(K^1L^n)$ and $\Gamma_L(K^1L^n)$ are not influenced by the L -shell vacancy configurations, and hence $\Gamma_K(K^1L^n)$, $\Gamma_L(K^1L^n)$, and $f_{n,n-1}$ can be replaced by Γ_K , Γ_L , and f , respectively, which are independent of n . Such an assumption is not unreasonable because in the exotic-atom experiment the L -shell refilling rates were not appreciably enhanced by the number of either L - or K -shell vacancies.¹¹ Then, in our experimental condition, i.e., $y_3^x \cong 0$, Eq. (1) can be reduced to the forms

$$y_0 = (1-f)^{-1}(\tilde{\omega}/\omega_0)[(1-f)y_0^x - f(\omega_0/\omega_1)y_1^x], \quad (2)$$

$$y_1 = (1-f)^{-1}(\tilde{\omega}/\omega_1)[y_1^x - f(\omega_1/\omega_2)y_2^x], \quad (3)$$

$$y_2 = (1-f)^{-1}(\tilde{\omega}/\omega_2)y_2^x, \quad (4)$$

and

$$y_0y_2/y_1^2 = {}_8C_0 {}_8C_2 / {}_8C_1^2 = \frac{7}{16}. \quad (5)$$

The relation (5) is deduced from the assumption that the primary vacancy distribution is binomial,¹² i.e., $y_n = {}_8C_n \tilde{P}_L(0)^n [1 - \tilde{P}_L(0)]^{8-n}$, where ${}_8C_n$ is a binomial coefficient and $\tilde{P}_L(0)$ is an average ionization probability at zero impact parameter. Here f can be determined by solving the quadratic equation (5) and $\tilde{P}_L(0)$ is also determined from the relation $y_1/y_2 = 8[1 - \tilde{P}_L(0)]/28\tilde{P}_L(0)$ if ω_1/ω_0 and ω_2/ω_0 are known.

When the ionicity becomes unity the electron configuration of F^- is considered to be the same as that of a Ne atom. Then ω_n/ω_0 or F^- in NaF ($I=0.91$) is now replaced approximately by that

of the Ne atom. Using the ratios $\omega_1/\omega_0 = 1.055$ and $\omega_2/\omega_0 = 1.222$ determined experimentally for Ne,¹³ we got $f = -0.032$ and $\tilde{P}_L(0) = 0.109$ for NaF. From the zero or almost zero probability of the L -vacancy rearrangement f for NaF we understand that no vacancy transfer occurs in highly ionic compounds.

For the fluoride with small ionicity where a degree of localization of a valence electron density on F^- is small and hence the wave function of the $F L$ shell cannot be replaced by that of Ne atom, the situation is more complicated and Eqs.

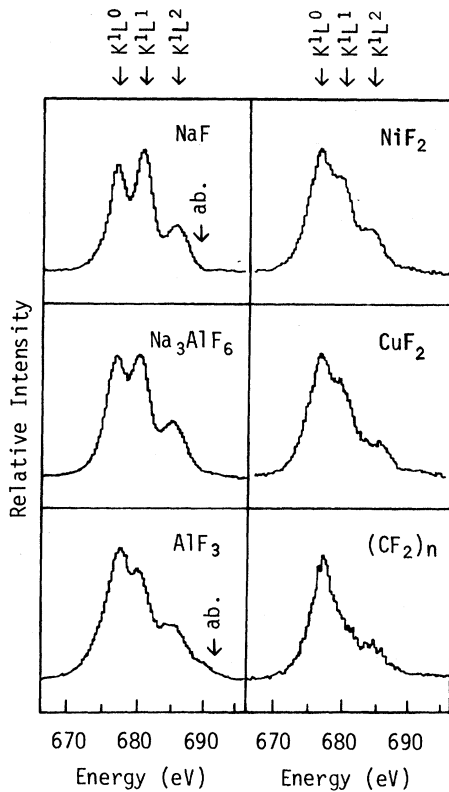


FIG. 1. F $K\alpha$ spectra of NaF, Na_3AlF_6 , AlF_3 , NiF_2 , CuF_2 , and Teflon $(\text{CF}_2)_n$ induced by 84-MeV N^{4+} . The arrows indicate the positions of the K absorption edges.

(2)–(5) cannot be used to evaluate f because ω_n/ω_0 for the fluoride deviates from that for the Ne atom. Such a deviation may be more significant for higher-order K^1L^n states but not for the K^1L^1 state. This is drawn from an analogy to the fact that the discrepancy between ω_n/ω_0 for the Ne atom, obtained with the statistical scaling procedure and with the exact Hartree-Fock-Slater calculation increases with n .¹⁴ On the other hand, the primary vacancy distribution y_n is considered to be less sensitive¹ to the change in the chemical environment under the condition where the direct Coulomb ionization process is dominant. Then in the case of small $\bar{P}_L(0)$ we can apply the same binomial distribution y_n , which is generated from $\bar{P}_L(0) = 0.109$ obtained with NaF, and the same $\omega_1/\omega_0 = 1.055$ obtained with the Ne atom to the fluorides other than NaF. f and ω_2/ω_0 can now be determined by solving Eq. (1) if we make the ratios y_0^x/y_1^x for f and y_2^x/y_0^x for ω_2/ω_0 using terms up to y_3 ($= 0.041$), as listed in Table I. f and ω_2/ω_0 increase with the covalency ($C = 1 - I$) as shown in Figs. 2(a) and 2(b). As Γ_K is less

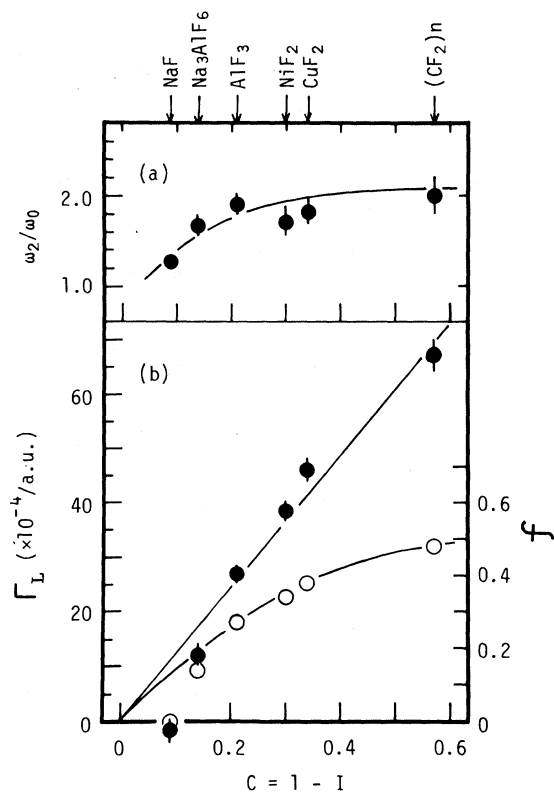


FIG. 2. The fluorescence yield ratio ω_2/ω_0 , the L -shell refilling probability f , and the L -shell width Γ_L plotted as a function of the covalency C for all of the fluorides examined. (a) Variation of ω_2/ω_0 with the covalency. (b) Variation of Γ_L (closed circles) and f (open circles) with the covalency.

sensitive than Γ_L to the change in the chemical environments we use the same Γ_K for all the fluorides. Γ_L is now estimated by using the theoretical value of $\Gamma_K(K^1L^0)$.⁸ Here a linear relationship between Γ_L and C can be seen in Fig. 2(b). Such a trend will be discussed in view of the bonding nature of the compounds.

The molecular-orbital (MO) wave function of the valence band of a fluoride MF is written as $\Psi(\text{MO}) = (1 + \lambda^2)^{-1/2}(\lambda\Psi_{M:F} + \Psi_{M+F-})$, where $\Psi_{M:F}$ and Ψ_{M+F-} are the wave functions associated with the covalent and ionic bonds, respectively. The covalency C is expressed as $\lambda^2/(1 + \lambda^2)$ which is a measure of delocalization of the valence electrons. Γ_L relates to a degree of the spatial overlap of the initial and final states of $\Psi(\text{MO})$. Then it can be deduced from the linear relationship between Γ_L and C that the vacancies produced in the F^- L shell transfer, only through the covalent character of $\Psi(\text{MO})$, to the valence bands of the

neighboring atoms. Further consideration of change in ω_1/ω_0 for F compounds with different chemical environments may improve ω_2/ω_0 here obtained. Study of the dependence of ω_1/ω_0 and ω_2/ω_0 on the covalency is in progress.

The chemical effect reflected in the intensity distributions of the $F K\alpha$ x-ray satellites produced by N^{4+} bombardment was observed and first explained quantitatively by introducing the vacancy rearrangement process in the L shell or the valence band of F^- . Γ_L estimated from the L -vacancy rearrangement probability f is directly proportional to the covalency. The technique offers promise for determining the ionicity or covalency of the chemical compounds with valence L -shell electrons.

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Intensity Correlations of a Cooperative System

G. S. Agarwal

School of Physics, University of Hyderabad, Hyderabad 500001, India

and

L. M. Narducci and Da Hsuan Feng

Department of Physics and Atmospheric Science, Drexel University, Philadelphia, Pennsylvania 19104

and

R. Gilmore^(a)

Physics Department, University of South Florida, Tampa, Florida 33620

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We suggest that the intensity correlation function could be an important tool in the study of atomic cooperative behavior because it contains predominantly components at $0, \pm 4\Omega$ in the limit of large Rabi frequency (2Ω) and large cooperation number. This is in contrast with the single-atom prediction where the intensity correlation function contains only frequency components at $0, \pm 2\Omega$. The master equation for the collective system is solved analytically in the secular approximation.

Many theoretical studies¹⁻⁷ of the cooperative effects in the interaction of atoms and molecules with a laser field and the vacuum of radiation have been carried out since the early work on superradiance by Dicke.⁸ Several manifestations of cooperative behavior have also been observed experimentally.⁹ In this Letter we discuss a commonly used model for the description of the collective behavior of two-level systems interacting with radiation in the context of resonance fluorescence. We show that the intensity correlation function^{10, 11} of the scattered light contains predominantly frequency components $0, \pm 4\Omega$ in the limit of large Rabi frequency (2Ω) and large cooperation number. This result is in contrast with the single-atom prediction which shows modulation only at frequency $\pm 2\Omega$ in the large-field