

K x-ray spectra of solid and gaseous fluorine compounds excited by 2-MeV/amu Ar and Mg ions

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The *K* α satellite and hypersatellite spectra of alkali-metal and alkaline-earth fluorides, excited by 80-MeV Ar ions, and the *K* α satellite spectra of a variety of gaseous fluorine compounds, excited by 48-MeV Mg ions, have been measured with a curved-crystal spectrometer. Analysis of these spectra using primary vacancy distributions deduced from spectra of Ne and HF, excited by the same projectiles, yielded rate constants for *L*-vacancy filling. The rate constants obtained from the satellite and hypersatellite distributions of the solid compounds are about the same (30×10^{-4} a.u.), but those obtained for the gaseous compounds are much smaller. A two-step mechanism involving electron transfer from outer levels of surrounding atoms to high-*n* states of the target atom, followed by subsequent *L* Auger decay is proposed.

I. INTRODUCTION

Systematic measurements of the spectra of fluorine *K* α x rays produced by the bombardment of alkali-metal and alkaline-earth fluorides with 5.5-MeV He and 22-MeV C ions have been reported previously.^{1,2} The spectra obtained with He ions provided clear evidence of resonant electron transfer to the fluorine *L* shell following *1s2p* ionization in the compounds KF and SrF₂. It was shown that such state selective electron transfer processes result from close energy matches between the pretransfer and post-transfer metal fluoride electron configurations. The spectra excited with C ions revealed that when higher stages of ionization are created, rapid electron transfer to the fluorine *L* shell occurs largely via a mechanism that is not state selective. Consequently, an overall depression of the intensities of the *KLⁿ* x-ray satellites for *n* > 2 is observed.

The exact nature of the mechanism for electron transfer in highly ionized atoms is still unknown. The fact that the effects of electron transfer are readily visible in *K* x-ray spectra means that the transfer process effectively competes with *K*-vacancy decay on a time scale of the order of 10^{-13} sec. Thus these transfer times are much shorter than typical valence electron transition lifetimes. They are, however, quite comparable to plasma frequencies in metals.

It is of interest to extend the investigations mentioned above to states of higher excitation. This is readily accomplished by examining the x-ray spectra produced by projectiles having charges significantly greater than the atomic number of the target. The measurements of Beyer *et al.*,³ as well as those presented in Ref. 4, demonstrate that when a 2-MeV/amu Ar ion undergoes a *K*-shell ionizing collision with a Ne atom, all but one or two electrons are stripped from the Ne atom. In the measurements to be presented herein, beams of 2-MeV/amu Mg and Ar ions were used to excite *K* x-ray emission in the series of alkali-metal and alkaline-earth fluorides studied previous-

ly with considerably lighter ions. In addition, measurements were performed on a number of gaseous fluorine compounds to investigate electron transfer in single molecules, and on HF to obtain spectra characteristic of free F⁻ ions.

II. EXPERIMENTAL METHODS

The experiments were performed using beams of 48-MeV Mg³⁺ and 80-MeV Ar⁵⁺ ions provided by the Texas A&M variable energy cyclotron. The Ar beam was used to obtain the spectra for the solid fluorine compounds whereas the Mg beam was used for the gas spectra because, at the gas pressures employed, interfering *L* radiation from Ar was produced at intensities comparable to the fluorine intensities. Targets of LiF, NaF, KF, MgF₂, CaF₂, and BaF₂ were made by vacuum evaporation onto 20- μ g/cm² carbon backing foils. The thickness of target material was 10 μ g/cm² or less as discussed previously in conjunction with the C-projectile measurements. The x-ray spectrometer was a Johansson type having a 12.7-cm focal circle radius and a curved thallium acid phthalate crystal. The geometry and other details were the same as described previously.²

Repetitive measurements with the same target showed that, during each measurement, the target became thinner. This effect was not found for C projectiles and is probably due to sputtering. Extremely high sputter rates have been observed recently for alkali halides under bombardment by high-energy heavy ions.⁵ Only the total x-ray intensities changed in the repeated measurements; the relative intensities of the individual satellite lines were not affected. The fluorine hypersatellites were measured using thick solid targets, since disturbing effects from the absorption edge were not expected. No sputtering effects were observed with the thick targets.

The gas measurements were performed on HF, SiF₄, SF₆, C₂F₆, CHF₃, and CHF₂CH₃ using a closed gas cell. The beam entrance window was a 1.9-mg/cm² Havar foil

and the x-ray exit window consisted of $65\text{-}\mu\text{g}/\text{cm}^2$ stretched polypropylene. In order to minimize self-absorption of the fluorine x rays in the gas, the distance between the beam axis and the x-ray window was 1.5 mm. The gas pressure was varied between 5 and 50 mbar, as measured by a mechanical diaphragm gauge, to check on self-absorption effects.

III. RESULTS

The spectra obtained for the alkali-metal and alkaline-earth fluorides from thin targets are compared in Fig. 1. The x-ray groups KL^0 to KL^7 appear in order of increasing energy. Rather large relative intensity differences occur for the first three satellite lines (KL^0 to KL^2) among the various compounds, whereas the higher satellite groups are rather similar.

In Fig. 2 a complete satellite and hypersatellite spectrum of KF, obtained with a thick target, is shown. As can be seen by comparison with the thin target spectrum, the influence of the absorption edge is not very great for this compound because of the high absorptive coefficient of potassium. For all the other compounds, the absorption of the metal ion is, in general, lower and the effect of the absorption edge is more significant. In the $K\alpha$ hypersatellite region, the peak of highest intensity arises from

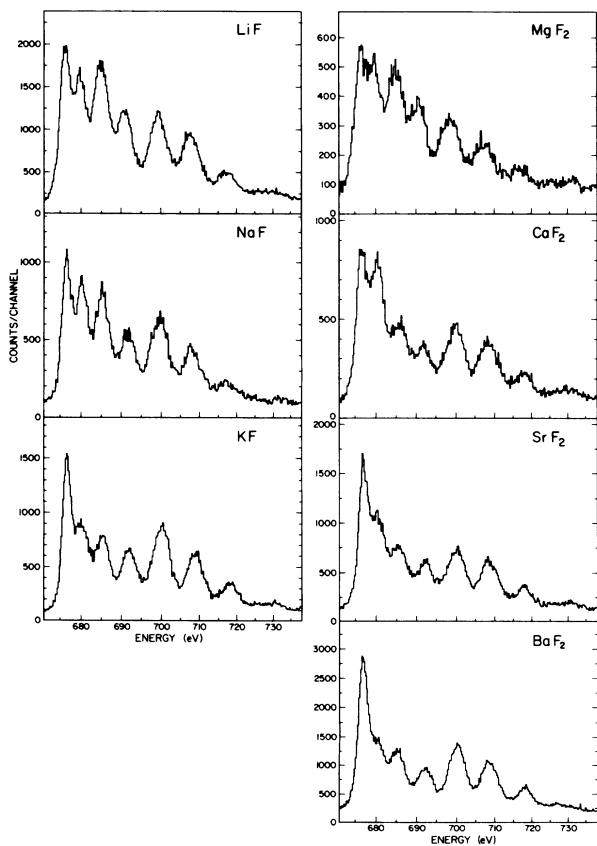


FIG. 1. Comparison of fluorine $K\alpha$ x-ray satellite spectra excited by 80-MeV Ar ions in thin targets of alkali-metal and alkaline-earth fluorides.

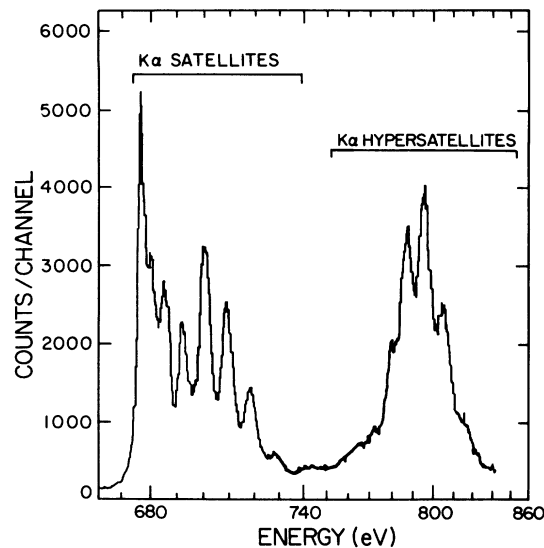


FIG. 2. Spectrum of fluorine $K\alpha$ satellites and hypersatellites excited by 80-MeV Ar ions in a thick KF target.

the K^2L^5 group. The K^2L^0 , K^2L^1 , and K^2L^2 groups have such low intensities that their peaks are not distinguishable. The $K\alpha$ hypersatellite peaks have about the same relative intensity distribution for all of the compounds.

A spectrum of the $K\alpha$ satellites excited in gaseous SiF_4 by 48-MeV Mg ions is shown in Fig. 3. The first line in this spectrum is 2 eV below the fluorine KL^0 energy observed in solid targets and originates from second-order diffraction of $1s2p(^1P)-1s^2$ transitions in He-like Mg projectile ions. The overall satellite intensity distribution in the SiF_4 spectrum is quite similar to those observed in the spectra obtained for the other gas, but is quite different from the distributions obtained for the solids (Fig. 2). The highest intensity satellite peak in the gas spectra is KL^5 .

A spectrum of fluorine K x rays excited by 48-MeV Mg ions in (gaseous) HF is shown in Fig. 4. The average state of ionization associated with this spectrum is much higher than those associated with the other gas spectra (Fig. 3). Here, the most prominent peaks are KL^6 and KL^7 , and

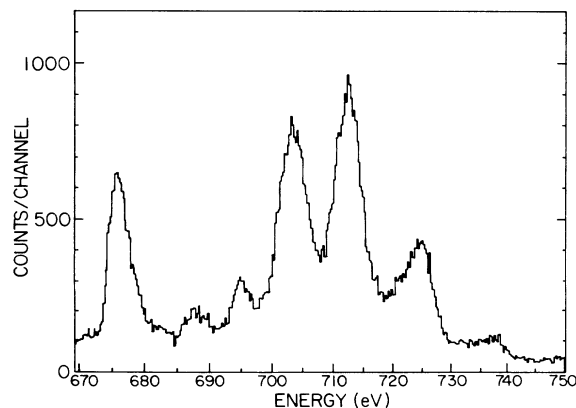


FIG. 3. Spectrum of fluorine $K\alpha$ satellites excited by 48-MeV Mg ions in a SiF_4 (gas) target.

both the 3P and 1P components of KL^7 are readily distinguishable. This spectrum is very similar to that obtained for Ne using the same projectile.⁴ The pressure dependence of the $^1P/{}^3P$ intensity ratio is shown in Fig. 5. The dotted line shows the results obtained previously for Ne by Beyer *et al.*³ As can be seen, the pressure dependence is essentially the same for both HF and Ne, but the limiting value of the HF intensity ratio deviates even more from the expected value of 1. This deviation may be caused by differences in the polarizations of the two transitions associated with alignment of the 3P and 1P states.⁶

All spectra were analyzed by means of a least-squares fitting program employing Voigt functions (FACELIFT). The procedure was the same as that described previously.² The peak intensities were corrected for crystal reflectivity and for absorption in the proportional counter window. The intensities obtained for the thin target spectra were corrected for intensity loss due to sputtering by assuming a linear decrease between repetitive measurements. In addition, components attributed to Ar projectile L x rays were subtracted from the thin target spectra using a spectrum of the projectile x rays excited by a thin carbon foil. The $K\alpha$ hypersatellite intensities obtained from the thick target spectra were corrected for self-absorption by the target. In the case of the gas spectra, only the satellite groups KL^4 to KL^7 were used for the evaluation to follow. These groups are well above the absorption edge and self-absorption corrections were negligible. Only corrections for absorption in the gas cell x-ray window were required in addition to the corrections mentioned above. The corrected intensities are listed in Table I.

IV. ANALYSIS

A. $K\alpha$ satellite spectrum of HF

Since there are no extra-atomic electrons available to F^- in this gas, L -vacancy filling is not expected to occur

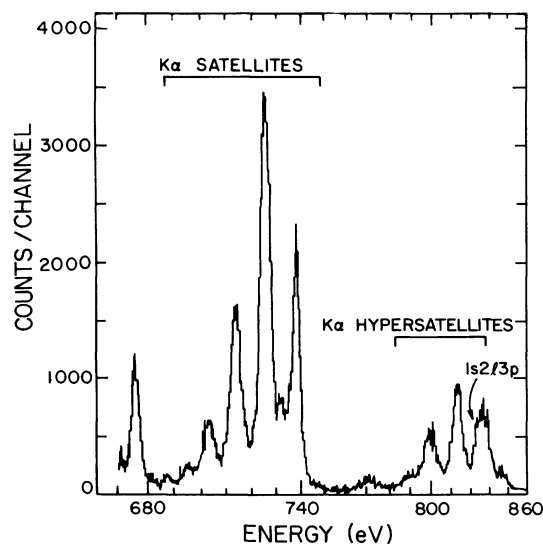


FIG. 4. Spectrum of fluorine $K\alpha$ satellites and hypersatellites excited by 48-MeV Mg ions in a HF (gas) target.

prior to K x-ray emission. The primary L -vacancy yield distribution was obtained (as for neon in Ref. 4) by correcting the satellite intensities for fluorescence yield.⁷ The distribution so obtained was nearly binomial with a p_L value of 0.70. The corresponding p_L value for Ne (0.66) is slightly lower as is to be expected since p_L decreases with increasing Z . The fact that the p_L values are nearly the same for Ne and HF is confirmation of the previous assumption² that the primary vacancy distribution of F^- can be accurately estimated from that for Ne.

B. $K\alpha$ satellite spectra of solid compounds

The intensity distributions in the spectra of Fig. 1 give the appearance of being composed of contributions from two different mechanisms. The lower- n satellites (KL^0 , KL^1 , and KL^2) are greatly enhanced compared to the higher- n satellites. Therefore, an analysis similar to that described in Ref. 2 was performed using only the intensities for KL^3 to KL^7 . In this analysis, it was assumed that the primary L -vacancy distribution is binomial with a p_L value of 0.78, as determined from the previous data obtained for 80-MeV Ar on Ne.⁴ Applying the formalism detailed in Ref. 2, values of the rate constants for electron transfer to the L shell were determined. They are listed in Table II. The error associated with each value is roughly estimated to be about $\pm 5 \times 10^{-4}$ a.u.

The calculated x-ray distributions for KL^3 to KL^7 , obtained using the λ_i from Table II, were in good agreement with the experimental distributions, and the individual peak intensities agreed to within 10%. As expected from the appearance of the spectra, the experimental KL^0 , KL^1 , and KL^2 intensities were considerably larger than those predicted from the above analysis. The magnitude of this effect can be shown by calculating the excess yield $E(n) = Y(n) - N(n)$ for each peak (KL^0 , KL^1 , and KL^2) where $Y(n)$ is the experimental relative yield of the KL^n peak and $N(n)$ is its calculated relative yield. The total enhancements $E = \sum E(n)$ are listed in the third column

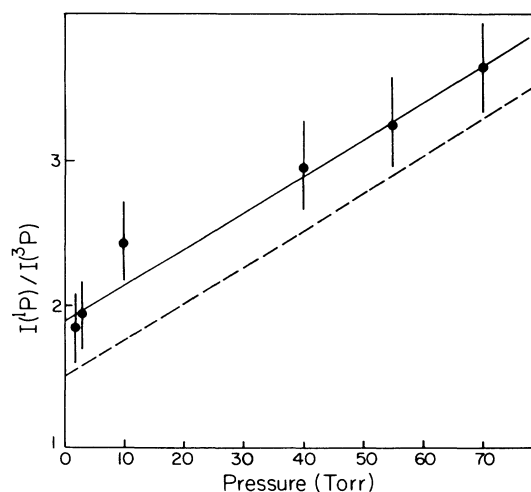


FIG. 5. Pressure dependence of the intensity ratio $I(^1P)/I(^3P)$ observed for HF. The dashed line shows the results of Beyer *et al.* (Ref. 3) for Ne.

TABLE I. Experimental relative intensities of fluorine $K\alpha$ satellites and hypersatellites (corrected for absorption and reflectivity).

Compound	KL^0	KL^1	KL^2	$K\alpha$ satellites		KL^5	KL^6	$KL^7(^3P)$	$KL^7(^1P)$
				KL^3	KL^4				
Solids									
LiF	0.165	0.112	0.191	0.137	0.138	0.119	0.055		0.026
NaF	0.162	0.137	0.177	0.135	0.171	0.119	0.056		0.035
KF	0.177	0.148	0.126	0.139	0.188	0.138	0.056		0.017
MgF ₂	0.131	0.147	0.221	0.135	0.144	0.120	0.062		0.039
CaF ₂	0.189	0.173	0.150	0.101	0.158	0.147	0.061		0.021
SrF ₂	0.212	0.147	0.157	0.121	0.155	0.135	0.058		0.013
BaF ₂	0.252	0.107	0.153	0.110	0.170	0.142	0.054		0.012
Gases									
HF				0.005	0.049	0.225	0.400	0.118	0.219
SiF ₄					0.340	0.419	0.208	0.013	0.021
SF ₆					0.362	0.377	0.266	0.025	0.071
C ₂ F ₆					0.306	0.388	0.231	0.022	0.054
CHF ₃					0.229	0.373	0.301	0.027	0.069
CHF ₂ CH ₃					0.337	0.372	0.233	0.022	0.037
$K\alpha$ hypersatellites									
Compound	K^2L^0	K^2L^1	K^2L^2	K^2L^3	K^2L^4	K^2L^5	K^2L^6	K^2L^7	
LiF	0.006	0.020	0.063	0.120	0.272	0.239	0.183	0.096	
NaF	0.005	0.014	0.049	0.117	0.270	0.259	0.189	0.098	
KF	0.011	0.026	0.035	0.117	0.279	0.238	0.185	0.064	
MgF ₂	0.009	0.027	0.071	0.135	0.277	0.235	0.154	0.093	
CaF ₂	0.014	0.030	0.048	0.116	0.277	0.259	0.180	0.076	
SrF ₂	0.010	0.031	0.050	0.125	0.289	0.284	0.154	0.059	

of Table II. Unlike the enhancements observed for the KL^0 in the carbon ion work (Ref. 2), the present enhancements do not show a discernable dependence on stopping power. About all that can be said is that the enhancements for the alkaline-earth fluorides are somewhat larger than those for the alkali-metal fluorides. It was found that the enhancement of KL^0 was always the largest contributor to the total enhancement, and that $E(0)$ was particularly large for the compounds KF, SrF₂, and BaF₂, where a contribution from resonant electron transfer is expected.² The exact cause of the enhanced KL^0 , KL^1 , and KL^2 intensities is not presently understood. One point of speculation is that additional contributions to these peaks result from K -electron transfer processes occurring in relatively large impact parameter collisions in which few L electrons are ionized.

TABLE II. Rate constants for electron transfer to the L shell (in units of 10^{-4} a.u.) and enhancements E (see text) obtained for the solid compounds.

Compound	λ_t	E
LiF	33.2	0.27
NaF	28.3	0.30
KF	26.2	0.27
MgF ₂	29.5	0.33
CaF ₂	18.7	0.42
SrF ₂	24.3	0.37
BaF ₂	23.4	0.38

C. $K\alpha$ satellite spectra of gaseous compounds

An analysis similar to that described above was performed on the intensity distributions (KL^4 to KL^7) obtained for the gaseous compounds. The resulting λ_t values are listed in Table III. Compared with the solids, the rate constants for the gases are much lower. Also, significant differences in the rate constants occur among the various gases.

D. $K\alpha$ hypersatellites of solid compounds

The analysis of the hypersatellites was carried out using theoretical x-ray and Auger transition rate constants which were averages over all the multiplets,⁸ since the individual multiplet transition rate constants were not available in the literature. When λ_t is significantly larger than the rate constants for x-ray and Auger decay (λ_x and λ_a), the above approximate procedure is not expected to introduce a significant amount of error [see Eqs. (4), (5), and (6) of Ref. 2].

The results are given in Table IV where it may be seen that the λ_t obtained for the $K\alpha$ hypersatellites are about the same as those for the $K\alpha$ satellites. Thus it appears that the electron transfer rate constants are relatively insensitive to the number of K holes. This result is consistent with the results of previous hypersatellite measurements using carbon ions⁹ if it is assumed that the total rate constant for K -vacancy decay of a double K -hole state is twice that of a single K -hole state.

TABLE III. Rate constants for electron transfer to the L shell (in units of 10^{-4} a.u.) obtained for the gaseous compounds.

Compound	λ_i
SiF ₄	10.2
SF ₆	3.8
C ₂ F ₆	6.2
CHF ₃	3.0
CHF ₂ CH ₃	8.1

V. DISCUSSION

It is interesting to find that the average λ_i value for electron transfer in the solid compounds excited by Ar ions (30×10^{-4} a.u.) is about the same as that obtained previously using carbon ions. This fact supports the assumption that $\lambda_i(n) = n\lambda_i$, since the primary vacancy distributions are quite different for these two cases. A rate constant of this magnitude yields L -vacancy filling probabilities of 0.87 and 0.97 for KL^5 and KL^6 , respectively.

Since the process responsible for L -vacancy filling of the highly ionized states produced in heavy-ion collisions does not appear to be a state selective (or resonant) one, other possibilities must be examined. Perhaps the electron transfer to the L shell occurs directly via interatomic Auger transitions, as has been suggested before.¹⁰ Alternatively, direct transfer of electrons from the outer np levels of surrounding metal ions to high-lying (Rydberg) states of the fluorine ion might occur via molecular orbital formation. Such a mechanism is known to be responsible for the population of high- n states of highly stripped, slowly recoiling ions in a gas target following bombardment with heavy-ion projectiles.¹¹ The transfer of electrons selectively occurs to states of the ions which match the energies of bound states in surrounding neutral target atoms. As an ion approaches a neutral atom, the potential barrier between the two partners decreases below the energies of the outer electrons of the neutral atom and allows electrons to transfer to the ion.

The latter mechanism requires a second step to fill L vacancies in the target atom. Namely, the high- n states, once populated, must decay to the L shell. The plausibility of this mechanism therefore relies heavily on the correspondence between the observed electron transfer rates and those expected for L Auger decay from $n \geq 3$ states. Unfortunately, reliable theoretical rates for the highly ionized states of interest here are not available. About the best that can be done is to use calculated rates for single vacancy states to get an order of magnitude estimate.

Consider a case in which there are three electrons in the L and M shells of a fluorine ion. Since Auger rates (per electron) are not very Z dependent, the K - and L -decay rates can be estimated from the Auger widths for atoms with equal numbers of L and M electrons. For $Z = 20$, the K Auger width is about 0.5 eV and the L Auger width is about 0.2 eV giving a ratio of L - to K -vacancy decay rates of 0.4.¹² Essentially the same conclusion is reached by comparing individual Auger transition rates. For ex-

TABLE IV. Rate constants for electron transfer to the L shell (in units of 10^{-4} a.u.) derived from the hypersatellite spectra.

Compound	λ_i
LiF	30
NaF	29
KF	33
MgF ₂	35
CaF ₂	33
SrF ₂	36

ample, the KL_2L_3 Auger rate for $Z = 25$ is 8.9×10^{-3} a.u. while the $L_2M_2M_3$ rate is 4.6×10^{-3} a.u. giving a ratio of 0.5.¹³ Taking the calculated average Auger decay rate of a KL^5 state of Ne (21×10^{-4} a.u.) (Ref. 7) and the above ratio of L - to K -decay rates yields a value of 10×10^{-4} a.u. as a rough estimate of the L -vacancy filling rate. Since this rate is comparable to the rates observed for the solid fluorine compounds, it is concluded that the two-step mechanism is indeed plausible.

As was noted in Sec. IV C, the L -vacancy filling rate constants obtained for the gases are much smaller than those obtained for the solid compounds. In this context, it is of interest to compare the lifetime of a K -hole state with the time it takes a highly ionized gas molecule to break apart. The mean lifetime of the KL^0 state of Ne is 2.6×10^{-15} sec, while for the KL^5 and KL^6 states it is 1.1×10^{-14} and 3×10^{-13} sec, respectively.⁷ The dipole allowed KL^7 (2^1P-1^1S) transition has a calculated lifetime of 1×10^{-13} sec.¹³ Hence it is evident that the transition lifetimes increase appreciably with the number of L vacancies, which is the reason that L Auger decay can effectively compete with K -vacancy decay in ions having depleted L shells if there are a few M -shell electrons present.

Two processes are responsible for molecular breakup: recoil of the target atom and Coulomb repulsion resulting from the high charge states produced in the collision. The recoil velocity imparted to a fluorine atom in a K -shell ionizing collision by a Mg projectile is estimated to be about 1.3×10^4 m/sec. If it is assumed that breakup occurs when the atom has traveled a distance of approximately 0.5 Å, the time required is about 4×10^{-15} sec. The separation time associated with a Coulomb explosion between two particles of charges q_1 and q_2 may be estimated using a formula given by Brandt and Ritchie.¹⁴ For charges $q_1 = +7$ and $q_2 = +4$, the formula predicts a time of 4×10^{-15} sec to increase the internuclear separation by 0.5 Å.

Of course, both of the above effects may cancel, but on the average they will complement each other. It seems reasonable, therefore, to expect the struck atom to have moved far enough to prevent electron transfer to energy matched states by virtue of the accompanying increase in the Coulomb barrier within a time period of the order of 10^{-15} sec. This means that there will be considerably less time for electron transfer to occur in gases than in solids, where neighboring atoms remain in close proximity to each other throughout the decay process.

VI. CONCLUSION

The fluorine $K\alpha$ satellite and hypersatellite spectra of solid ionic fluorine compounds, excited by 80-MeV Ar ions, and the satellite spectra of gaseous fluorine compounds, excited by 48-MeV Mg ions, have been examined. Comparison of these spectra with spectra for Ne and HF excited by the same projectiles revealed that L -vacancy filling prior to K -vacancy decay occurs with a probability of the order of 95% for highly ionized states such as KL^6 . A single L -vacancy filling rate constant of about 30×10^{-4} a.u. was found to characterize both the satellite and hypersatellite intensity distributions for the solid compounds reasonably well. The intensities of the KL^0 , KL^1 , and KL^2 peaks in the spectra of the solids appeared to be considerably enhanced. The cause of this effect is not yet understood.

A two-step mechanism was proposed to explain the high electron transfer probabilities in solids. This mecha-

nism involves the transfer of electrons from the outer levels of surrounding atoms to energy matched high- n states of the highly ionized target atom, followed by subsequent Auger decay to the L shell.

The spectra for the gaseous compounds were characterized by much smaller L -vacancy filling rate constants than those found for the solids. In terms of the proposed two-step mechanism for electron transfer, it is likely that the fast breakup of gaseous molecules lowers the probability of electron transfer into high- n states of the target atom.

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