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PHYSICAL REVIEW A VOLUME 4, NUMBER 1 JULY 1971

Energy Shifts Observed in Ni K X Rays Produced by Fission-Fragment Collisions*

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The $K\alpha$ and $K\beta$ x rays of Ni produced by the passage of light fission fragments from the spontaneous fission of ^{252}Cf through a thin Ni foil were found to be shifted up in energy by 69 ± 11 and 210 ± 16 eV, respectively, relative to the x rays produced by 6-MeV α particles and by photons from the decay of ^{241}Am. These shifts are similar in character to those observed previously in 15-MeV oxygen-ion bombardments, but require extremely high ionic charge states to be explainable in terms of multiple inner-shell plus outer-shell ionization.

I. INTRODUCTION

A study of x rays produced by the passage of fission fragments through matter, in which a cyclic dependence of the K- and L-shell ionization cross sections on the atomic numbers of the collision partners was observed, has previously been reported by Specht.[1] Recently, a similar Z dependence of x-ray production cross sections has been observed by Kavanagh *et al.*[2] in ion-atom collisions between Cu and a wide range of heavy-ion projectiles having energies below approximately 10 keV/amu. These data have been interpreted as evidence for a mechanism in which inner-shell vacancies are produced by the promotion of electrons as a result of the crossing of quasimolecular states formed during collision. A model for this mechanism has been discussed by Fano and Lichten[3] and by Specht.[1]

Energy shifts have recently been observed by Burch and Richard[4] in K x rays emitted as a result of 15-MeV oxygen-ion bombardments of Ca and V. These authors present evidence that multiple inner-shell ionization may be the cause of the observed x-ray energy shifts, but argue against the quasimolecular model from the point of view that the adiabatic approximations necessary in the quasimolecular model are not expected to be valid at these energies (~ 1 MeV/amu).

In his study of x-ray emission induced by fission fragments, Specht also noted energy shifts in the gross spectra of K and L x rays. In order to determine whether the x-ray energy shifts resulting from fission-fragment-induced x-ray emission display the same characteristics as those observed in the oxygen-ion bombardments, we have carried out a detailed examination, under high resolution, of the Ni K x rays produced by the passage through a thin Ni foil of fission fragments emanating from a source of ^{252}Cf. The results of this investigation

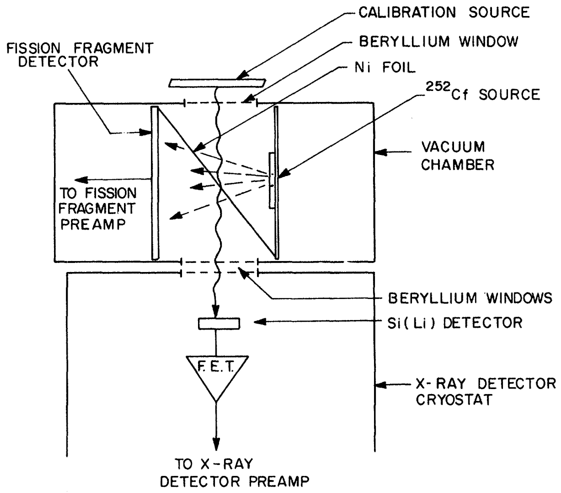

FIG. 1. Schematic diagram of the experimental arrangement.

are reported herein.

II. EXPERIMENTAL

A schematic diagram of the experimental arrangement is shown in Fig. 1. The experiments were carried out using a Si(Li) x-ray spectrometer giving a system resolution of 300 eV full width at half-maximum (FWHM) at 6.4 keV under conditions of the measurements. A 2.54-cm-diam metallic Ni foil of 2.79 mg/cm^2 thickness was mounted at a 50° angle coaxially between a ^{252}Cf source (giving a fission rate of approximately 1.2×10^5 fissions/min) and a 2.0-cm-diam silicon surface barrier fission-fragment detector. All of these components were contained inside a small vacuum chamber which was separated from the x-ray detector cryostat by two 0.025-cm-thick beryllium windows. Both the californium source and the fission-fragment detector were located at a distance of 0.75 cm from the Ni foil. The x-ray detector was positioned at 90° with respect to the source-foil-fragment detector axis and centered with the Ni foil at a distance of 1.52 cm.

The two detector outputs were analyzed by a standard fast-slow coincidence system in which it was required that an x ray and a fission fragment be detected within 100 nsec of each other. The lower-level discriminator of a single-channel analyzer was set to eliminate from the coincidence circuitry pulses originating in the fission-fragment detector of up to twice the pulse height produced by the 6-MeV α particles arising from the α-decay mode of ^{252}Cf. It was estimated from range-energy data[5,6] and fission-fragment pulse-height defect data[7] that only fission fragments of $Z < 50$ produced acceptable pulses in the fission-fragment detector after passing through the Ni foil. This corresponds to essentially the entire distribution of light fission fragments produced in the fission of ^{252}Cf of which ^{107}Tc is the fission fragment having the highest yield.[8] The average energy of these fragments during their passage through the Ni foil is estimated to be 59 MeV. The x-ray pulses which satisfied the coincidence requirements were sent to a 2048-channel analyzer and stored in a 1024-channel segment of the analyzer memory. The coincidence rate was approximately 29 counts/min.

At regular intervals throughout the experiment, counting was interrupted and an energy calibration was carried out. The energy calibration was accomplished by recording the spectra of x rays emitted in the decay of ^{57}Co and ^{241}Am from calibration standards placed at a beryllium window port located on the side of the vacuum chamber opposite to the x-ray spectrometer. X rays from these sources had to pass through the Ni foil in order to reach the x-ray detector and hence it was possible to record the spectrum of Ni x rays fluoresced by photons from the ^{241}Am source simultaneously with the ^{241}Am calibration. Upon completion of the fission-fragment bombardments, the single-channel analyzer discriminators were set to accept only pulses equivalent to those produced by the 6-MeV ^{252}Cf α particles and the spectrum of Ni x rays in coincidence with these α particles was recorded.

III. RESULTS AND DISCUSSION

In Fig. 2 is shown a comparison of the Ni x-ray spectra produced by (a) fission fragments, (b) α particles, and (c) photons. It is apparent that the $K\alpha$ and $K\beta$ lines in the Ni x-ray spectrum resulting from the fission-fragment bombardments are con-

TABLE I. Results of least-squares spectral analysis of Ni x rays produced by fission fragments, α particles, and photons. The energies E and the peak FWHM Γ are in units of eV. The specified errors are standard deviations obtained from the values of each parameter in two or more independent determinations.

Projectile	$E_{k\alpha}$	$\Gamma_{k\alpha}$	$E_{k\beta}$	$\Gamma_{k\beta}$	$I_{k\beta}/I_{k\alpha}$	$E_{k\beta} - E_{K\alpha}$
Fission fragments	7532 ± 5	351 ± 1	8450 ± 12	646 ± 16	0.098 ± 0.005	918 ± 13
α particles	7460 ± 10	325 ± 6	8242 ± 11	349 ± 5	0.143 ± 0.002	782 ± 14
Photons	7466 ± 10	316 ± 6	8238 ± 10	364 ± 6	0.153 ± 0.002	772 ± 14

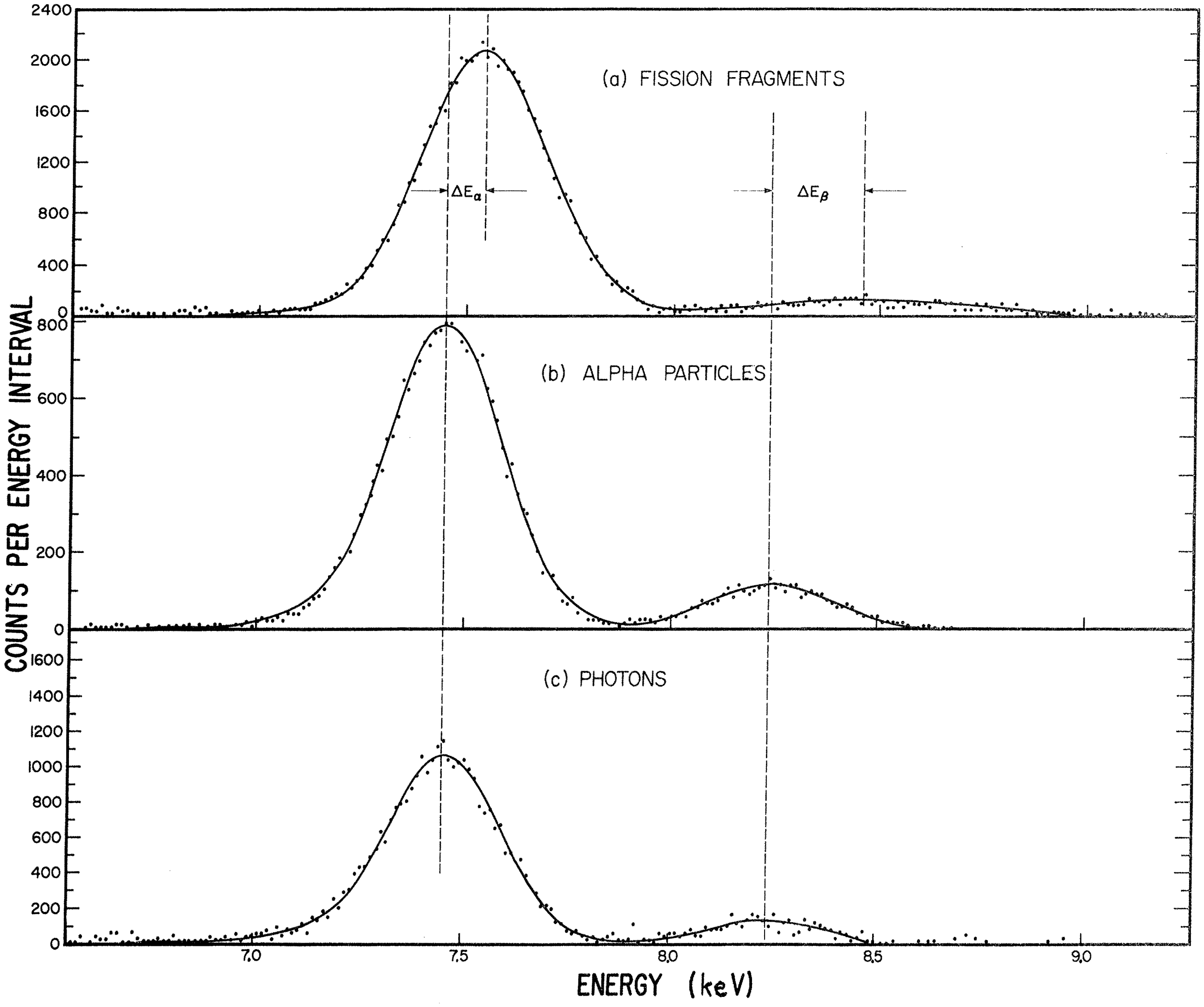

FIG. 2. Comparison of the spectra of Ni K x rays produced in bombardments with (a) fission fragments, (b) α particles, and (c) photons. A least-squares fitted background has been subtracted from each of these spectra.

siderably shifted and broadened compared to the Ni x-ray spectra obtained by α particles and photons. A reduction in the $K\beta/K\alpha$ intensity ratio is also observable in spectrum (a). Qualitatively, the peak shifts and increased widths are very similar to those observed by Burch and Richard in the K x-ray spectra of Ca and V resulting from 15-MeV oxygen-ion bombardments.

Each of the x-ray spectra (including the energy calibration spectra) was analyzed with a computerized least-squares peak and background fitting procedure in which the $K\alpha$ and $K\beta$ x-ray groups were represented by Gaussian functions having exponential tails. From this analysis, peak centroids, areas, and widths were determined and energy calibrations were obtained from least-squares fits of the calibration peak centroid-versus-energy curves. The results of the least-squares analysis is given in Table I. The Ni $K\alpha$ and $K\beta$ groups are shifted up in energy by 69± 11 and 210± 16 eV, respectively, and the $K\beta/K\alpha$ intensity ratio is reduced by (33.8± 0.5)% for fission-fragment-induced x-ray emission relative to the averages obtained for α-particle- and photon-induced x-ray emission. These shifts are somewhat larger than the average $K\alpha$ shift of 53± 6 eV and average $K\beta$ shift of 157± 6 eV reported by Burch and Richard for Ca and V x rays. The weighted average shift ($\langle \Delta E_{\alpha,\beta} \rangle = 82$ eV) is in good agreement with the shift observed by Specht in the unresolved Ni K x rays (≈ 90 eV).

Hartree-Fock-Slater calculations were carried out to ascertain whether the x-ray energy shifts ob-

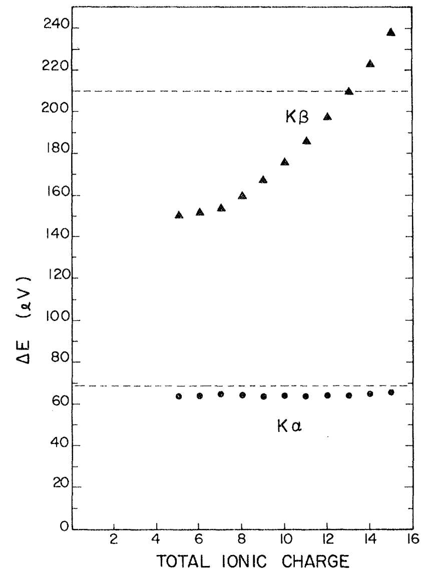

FIG. 3. Calculated $K\alpha$ and $K\beta$ x-ray energy shifts for the ion configuration $(1s^{-1})$ $(2s^{-1})$ $(2p^{-1})$ $(3p^{-2})$ of Ni as a function of total ionic charge. The dashed lines indicate the experimentally observed x-ray energy shifts.

served in the present study are consistent with the shifts predicted for atoms having multiple inner-shell plus outer-shell ionization as was the case for the oxygen-ion data. Using the computer program of Herman and Skillman,[9] approximate Ni x-ray energy shifts were calculated by taking the differences between the x-ray energies obtained from the appropriate orbital energies for the ion state of interest and those for a Ni atom having one K-shell vacancy. The results of these calculations for the ion configuration $(1s^{-1})$ $(2s^{-1})$ $(2p^{-1})$ $(3p^{-2})$ as a function of total ionic charge are shown in Fig. 3. The total ionic charge is the sum of the number of inner-shell vacancies (in this case 5) plus the number of outer-shell electrons which have been removed. The dashed lines indicate the experimentally observed x-ray energy shifts. Qualitatively, the rather large change in $\Delta E_{K\beta}$ as outer-shell electrons are removed is consistent with the observed relative peak broadenings on the assumption that a range of ionic charge states are produced. Various other ion configurations were found to give estimated $K\alpha$ and $K\beta$ shifts in agreement with experiment and those involving the simplest inner-shell configurations are summarized in Table II. These calculations indicate that the experimental shifts can be reproduced by removing various combinations of inner- plus outer-shell electrons, but that extremely high ionic charge states are required. On the average, a total ionic charge of +12 to 13 is needed to give the correct calculated $K\beta$ shift. The configurations which involve missing $3p$ electrons could account for the observed reduction in the $K\beta/K\alpha$ intensity ratio.

In conclusion, $K\alpha$ and $K\beta$ x-ray energy shifts have been observed in Ni x rays induced by fission-fragment collisions. These shifts are found to be similar in character to those previously observed in 15-MeV oxygen-ion bombardments, but require the postulation of extremely high ionic charge states in order to be explained by multiple inner-shell plus outer-shell ionization. The general similarities between the x-ray energy shifts observed in fission-fragment bombardments and 1-MeV/amu

TABLE II. Ion configurations of Ni estimated to give x-ray energy shifts in agreement with experiment. The listed energy shifts are calculated shifts (in eV) averaged over the range of ionic charge states specified.

Core excitation state		Total ionic charge	$\langle\Delta E_{k\alpha}\rangle$	$\langle\Delta E_{k\beta}\rangle$
$(1s^{-1})$ $(2s^{-1})$ $(2p^{-1})$		12–15	59	214
$(1s^{-1})$ $(2p^{-2})$		10–14	67	211
$(1s^{-1})$ $(2s^{-1})$ $(2p^{-1})$	$(3s^{-1})$	12–15	61	213
	$(3s^{-2})$	12–15	63	213
$(1s^{-1})$ $(2s^{-1})$ $(2p^{-1})$	$(3p^{-1})$	11–15	61	209
	$(3p^{-2})$	11–15	65	211
	$(3p^{-3})$	11–15	69	214
	$(3p^{-4})$	11–14	73	211
	$(3p^{-5})$	10–14	78	208
$(1s^{-1})$ $(2p^{-2})$	$(3p^{-1})$	10–14	70	214
	$(3p^{-2})$	10–13	75	211
	$(3p^{-3})$	10–13	79	214
$(1s^{-1})$ $(2s^{-2})$	$(3p^{-3})$	13–15	59	209
	$(3p^{-4})$	13–15	64	212
	$(3p^{-5})$	12–15	68	208

oxygen-ion bombardments, along with the previously observed similarities in the cyclic Z dependence of ionization cross sections for fission fragments and 10 keV/amu heavy ions, suggest the possibility that both phenomena are linked to the same mechanism and that this mechanism is the dominant one for the production of x rays by heavy ions over the whole range of energies extending from approximately 10 keV/amu to 1 MeV/amu.

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Nonlinear Temperature Dependence of F^{19} Chemical Shifts in CF_4 and SiF_4 Gases*

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Precise F^{19} NMR chemical shift measurements have been made on gaseous CF_4 and SiF_4 at different temperatures and pressures and a distinct nonlinear temperature dependence has been found. It is shown that this effect can be adequately explained with the help of a London dispersion field and a field due to repulsion. Present work is compared with Xe^{129} results.

I. INTRODUCTION

NMR chemical shifts in pure gases and their mixtures have been used recently by a number of investigators[1–3] to study intermolecular interaction effects. H^1 and F^{19} chemical shifts have been found to be linearly dependent on density, unlike Xe^{129} shifts which have also quadratic[3,4] and cubic[3] density dependence. Density and temperature dependences of F^{19} chemical shifts in gaseous CF_4 and SiF_4 are reported here. The density dependence is strictly linear as found earlier except the slope in the chemical shift versus density plot has changed considerably in the present work owing to better experimental techniques. The temperature dependence of F^{19} chemical shifts is found to be nonlinear and this has not been previously studied by NMR. These effects have been explained here in terms of long-range and short-range contributions to screening.

II. EXPERIMENTAL

A gas-tight sample tube has been designed that is satisfactory for NMR studies up to pressure 60 atm and temperature 350 °K. The detailed design of such a tube is given elsewhere.[2] The gases investigated here were obtained from Matheson of Canada Ltd. (minimum purity stated: CF_4 99.7% and SiF_4 99.6%). The F^{19} NMR absorption spectra were recorded on a Varian 60-MHz spectrometer operating at 56.445 MHz by the field-lock frequency-sweep method. The locking and sweeping frequencies were stable to 0.1 Hz throughout the operation. The frequencies were calibrated using an electronic counter. An external audio oscillator was used for locking the reference signal in the case of SiF_4 gas. The measurements were performed in the pressure range of 5–60 atm and temperature range of 223–350 °K. The Varian V-4341 variable temperature system was used for the temperature studies. This unit was calibrated properly before its use. The temperatures are accurate within ± 1 °K. Gas was always transferred at low pressure and densities were determined by assuming ideality and are known to better than 1%. The chemical shifts measured in CF_4 and SiF_4 were