ical, and radiochemical behaviors of homologous elements; and it holds promise of a large concentration factor. Previous searches for superheavy elements in nature have been undertaken with fewer encouraging signs.

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Outer-Shell Rearrangement in Highly Stripped Core Ions in Molecules*

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In observing the resolved $K\alpha$ x-ray satellite structures of Si and S from various molecular gas targets induced by O and Cl beams, we find shifts in relative intensity and centroid energy for the individual satellites indicative of substantial outer-shell relaxation prior to K-hole filling.

We report in this Comment high-resolution measurements of K x rays emitted by highly stripped Si and S ions residing in molecular environments which show effects attributable to massive outer-shell rearrangement within the K-hole lifetimes. Using 29.6-MeV O and 53.4-MeV Cl beams to produce single K-multiple L vacancy configurations in the gases SiH_4, SiF_4, H_2S, and SF_6, we find appreciable downward shifts in both the center of the $K\alpha$ satellite intensity distribution and the energy centroids of the individual satellites for the multivalence electron SiF_4 and SF_6 molecules as compared to the few valence electron molecules. The shift of emission strength to the lower energy satellites is reasonably well reproduced by a simplified L cascading model in which prior relaxation governed by the valence-shell occupancy is assumed. The dramatic dependence on satellite configuration of the energy shifts, indicative of valence-electron screening, lends added support to the assumption.

The need for the detailed understanding of the relaxation schemes is apparent from the study of such effects in solids[1,2] as well as considerations of the interactions of highly charged heavy ions with less dense electron environments, e.g., plasmas. Our investigation of relatively simple and isolated systems such as single molecules should help provide a basis for characterizing the processes which are involved in the more complex situations.

Ion beams of O and Cl were provided by the Stony Brook FN tandem Van de Graaff accelerator. The beams were collimated to 1 mm and then passed through an enclosed gas cell with 500-$\mu g/cm^2$ Ni entrance and exit foils. These foils were situated approximately 2 cm apart, framing the viewing region for a Bragg curved crystal spectrometer. A 0.0125-mm-thick Mylar window capping the side of the cell toward the spectrometer maintained vacuum separation from the beam line and spectrometer, which had a common vacuum. An ammonium dihydrogen phosphate crystal was used, with a flow mode proportional counter serving as the detecting element. K x-ray signals were processed with a single-

channel analyzer and stored for fixed periods of beam charge integration by means of a multiscaling analyzer. Stepping of the crystal was controlled automatically by an electronic unit.

Target pressures from 10 to 40 Torr were established in the cell, as measured by a mechanical diaphragm gauge, with no change in beamline pressures which were in the 10^{-6}–10^{-5} Torr range. The initial beam energies were 32 MeV O and 60 MeV Cl, with energy degradation to 29.6 and 53.4 MeV, respectively, due to the Ni entrance foil. Separate measurements with solid targets of thick Si and 150 $\mu g/cm^2$ CdS at the same collisional energies provided calibration lines and standards for comparing the various aspects of the gas spectra. The gas cell was removed for scans with solid targets; however, the collimator achieving beam definition was fixed so as to insure the same geometry for gas and solid runs. Beam currents were 20 nA or less for all runs.

The spectra produced by Cl incident on 20 Torr of SiH_4 and 40 Torr of SiF_4 are shown in Fig. 1. No dependence of the structure on the pressure in the range 10–40 Torr was observed. The lower pressure for the SiH_4 was necessitated by the rapid deterioration of the Ni foils, which under penetration by 10 nA of beam would last only a few hours. In each case, the spectrum consists of a group of peaks, each of which is associated with[1,2] states arising primarily from a configuration with one K vacancy and a number "n" of L vacancies, denoted KL^n. The shifts mentioned above are evident in the Fig. 1. More quantitative information is contained in Fig. 2 which displays the results of the least-squares fitting of the spectra with a series of Gaussians superimposed on a linear background. The differences
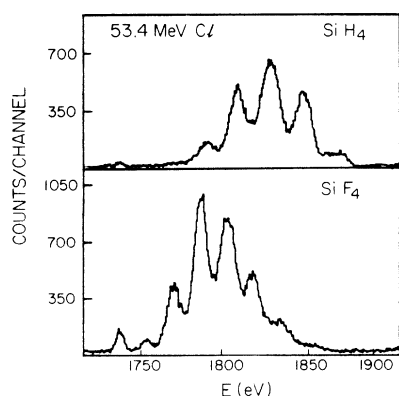
between the centroid energies in the gas spectra and the corresponding values in the solid spectra are exhibited in Figs. 2(a) and 2(d) for Si and S, respectively. In addition results for the shifts of Si using the O beam are included in Fig. 2(a). Complete results for O will be communicated elsewhere. The relative intensities resulting from Cl bombardment of the gas and solid targets are presented in Figs. 2(b) and 2(e) in fractional form $R_x{}^n$. The errors in the energy shifts are all less than ±0.3 eV, except for the highest satellites in each case, for which the uncertainties are about ±1.0 eV. For the intensities, the errors are ~15% for the weaker lines and ≲5% for the stronger peaks.

The main features of the SiH_4 spectrum agree quite well with previous data[2] taken with an equilibrated 45-MeV Cl beam passing through a thin gas target. As seen in Fig. 2(b), the intensity distribution is shifted well above and is much narrower than that for the solid while the individual satellite positions are seen in Fig. 2(a) to be shifted to a degree consistent with essentially a total

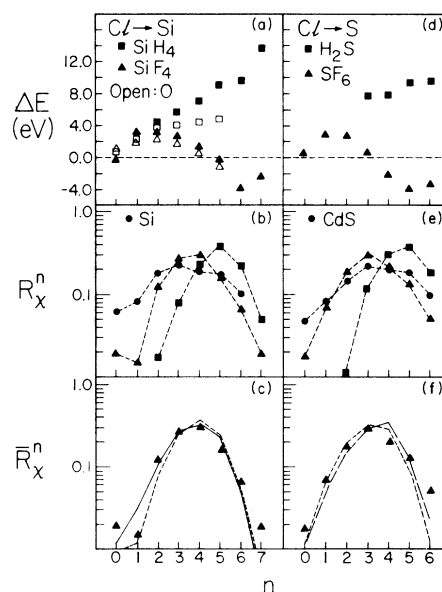FIG. 1. Si $K\alpha$ x-ray spectra induced in SiH_4 and SiF_4 by 53.4-MeV Cl ions.

FIG. 2. The centroid energy shifts and relative intensities of the $K\alpha$ x-ray satellites. (a) Centroid energies in gases relative to those in solid for Si arising from Cl (filled symbols) and O (open symbols) bombardments. (b) Relative intensities of Si $K\alpha$ satellite lines for SiH_4 (squares), SiF_4 (triangles), and solid Si (circles) induced by Cl with the dashed curves drawn merely to indicate trends. (c) Comparison of the "relaxed" satellite intensity distribution $\bar{R}_x{}^n$ for Si (curves) with SiF_4 data (see text for details). The corresponding results for S using Cl on H_2S, SF_6, and solid CdS targets are displayed in (d), (e), and (f).

loss of screening due to completely ionized valence shell.[2] In contrast the SiF_4 spectrum demonstrates a distinct reversal of those trends. Here the intensity distribution, while again much narrower, is centered fairly close to that for the solid. The centroid positions, initially tracking those of SiH_4, invert and actually become negative for the higher satellites. An analogous situation regarding yields and shifts is found for S using H_2S and SF_6 [see Figs. 2(d) and 2(e)].

In interpreting the observations, we make the assumption that the beams involved in the collisions have essentially the same charge state distribution for all of the gases and hence produce initially the same distributions of KL^n vacancies for, say, SiH_4 and SiF_4 in the collisions. Although some re-equilibration of the Cl to a lower mean charge in the gas is expected, the process should be similar for different gases, toward a semiempirical equilibrium value[3] of 11.1. The agreement between the present SiH_4 results and those taken[2] under single collision conditions indicates that our assumption is reasonable. Thus the differing features of the spectra are attributed to rearrangement in the multivalence molecules following incomplete ionization of the valence electrons. This assertion is supported further by the similarity of the energy shifts obtained using O, a significantly different projectile, on the same set of targets. To set the stage for further amplification, we note that both the projectile transit time and the valence-electron response time are much shorter than the K-hole lifetime. Thus, following the massive removal of the core-atom's inner-shell electrons, the un-ionized valence electrons would cluster around the highly charged core ion, helped along by the Coulomb explosion which pushes the constituent ions slightly apart and the relatively lesser attraction of the peripheral ions due to their filled inner shell. This provides us with the rationale to treat the core ion in isolation and the valence electrons as the M electrons.

Consider now the specific case of Si. First we obtained the L vacancy distribution from the x-ray distribution for SiH_4 and take it to be representative of the distribution created initially in the collisions, since the lack of M electrons precludes L relaxation. Neglecting KL^8 for which we have no information and which should be of minor importance according to the x-ray spectrum, the vacancy distribution is given by

$$R^n = (R_x{}^n/\omega_n)/\sum_{n=0}^{7} (R_x{}^n/\omega_n), \qquad (1)$$

where the fluorescence yield ω_n for the nth satellite is scaled up from that calculated[4] for Al. The "relaxed" distribution for SiF_4 is then, because of the rearrangement in the presence of M electrons,

$$\overline{R}^n = (R^n + \sum_{m=n+1}^{7} R^m P_{mn})(1 - P_{n(n-1)}), \qquad (2)$$

$$\overline{R}_x{}^n = \overline{R}^n \omega_n /(\sum_{n=0}^{7} \overline{R}^n \omega_n), \qquad (3)$$

where P_{mn} is the probability that the mth configuration is transformed to the nth configuration via L filling before the K vacancy is filled. Using a cascading approximation,

$$P_{mn} = P_{m(m-1)} P_{(m-1)(m-2)} \cdots P_{(m-n+1)n}, \qquad (4)$$

$$P_{n(n-1)} = \lambda_L{}^n/(\lambda_L{}^n + \lambda_K{}^n). \qquad (5)$$

Here $\lambda_L{}^n$ and $\lambda_K{}^n$ are the average L and K filling rates, respectively, for the nth satellites. The values for $\lambda_K{}^n$ have also been estimated from those[4] for Al. As no calculations or data currently exist concerning the L rates for multiple L vacancy configurations, we have made a statistical assumption that $\lambda_L{}^n$ is equal to $n\lambda_L{}^1$, where $\lambda_L{}^1$ is the single vacancy rate corresponding to KL vacancy. For this particular case, the constant $\lambda_L{}^1$ itself should be larger than that[5] of a single L vacancy. For the results we show here, we simply take a multiple of the calculated[5] single-vacancy rate. A second question is the degree to which the M shell is populated, since the availability of those electrons directly determines the rates. The solid curve in Fig. 2(c) was generated for the relaxed x-ray distribution $\overline{R}_x{}^n$ using twice the theoretical single-vacancy rate for the nth satellite derived from a statistically weighted average of the λ_1 and $\lambda_{2,3}$ rates[6] and no adjustment for the depletion of M electrons through cascading, which is equivalent to assuming that the M vacancies are refilled. If one takes a fixed number of available M electrons (8, for example) and requires depletion along with the appropriate reduction in the rates in the cascading rearrangement, the dashed curve in Fig. 2(c) is obtained. The important thing to notice is that regardless of the specific scheme employed, the approximate location and the width of the distribution compare favorably with the SiF_4 data points. Even the use of the single value of the theoretical rate for all configuration works well, yielding a set of points only slightly shifted up from the dashed line.

An identical treatment of the S using fluores-

cence yields ω_n and K rates $\lambda_K{}^n$ scaled down from calculations[7] for Ar gives equally good agreement. Taking the initial distribution to be the H_2S spectrum, the dashed curve in Fig. 2(f) was obtained assuming an initial number of twelve M electrons and allowing depletion, starting with $\lambda_L{}^1$ equal to twice the single-vacancy rate.[5] The long dashed curve represents the use of the single-vacancy rate with no depletion. Again, both approaches emulate the SF_6 points.

The simple model is seen to give a good account of shifts in intensity. The relative insensitivity to the assumed M populations is due to the dominance of the L rate over the K rate for the higher n satellites. However, the depletion scheme is more realistic and is reflected in the data on energy shifts. For the specific case of SiF_4, comparisons with computed Hartree-Fock energies[8] for a free atom with defect configurations of the type $1s(2s2p)^n 3s^2 3p^m$, where $m = 0$, $1, \ldots 6$, yield M numbers of ~ 4, 5, and 5 electrons for the KL^5, KL^6, and KL^7 groups, respectively, in contrast to ~ 2 for KL^2. With the assumption of equal initial M populations, the depletion scheme requires only a difference of ~ 1 between the KL^5 and KL^2 satellites as compared to ~ 2 deduced above. This would suggest that the more highly charged central ions are attracting more electrons from the bonding partners. More definitive conclusion on this effect would require improved calculations for the energy

shifts in which the effects of the fragmented ions are taken into account.

In conclusion, we have observed in high-resolution heavy-ion-induced $K\alpha$ x-ray satellite spectra evidence for substantial outer-shell rearrangement in highly stripped ions within single molecules which occur within K-hole lifetimes ($\geqslant 1.5 \times 10^{-15}$ sec) and apparently before the fragments move appreciably apart due to Coulomb explosion between stripped partners. The technique offers promise for testing valence-electron responses to other highly charged members within molecular systems, such as peripheral ions rather than core ions.

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