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Anomalous Spectral and Yield Features of Auger Emission from Symmetric Molecules

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Proton-induced sulfur *LMM* and carbon *KLL* Auger yields from SF_6, CF_4, and CCl_4 gaseous targets are found to be substantially reduced from the corresponding yields observed using H_2S, SO_2, and CH_4. Speculations about the observed dependence on chemical species include inelastic scattering of the Auger electron during its transit out of the molecule and double Auger emission to the continuum.

In this Letter we report the first observation of a significant dependence of the Auger-electron emission cross section on the chemical species of a molecular gas which is ionized by fast protons. We present qualitative arguments for the idea that the Auger electron from a core-location atom undergoes inelastic scattering off neighboring atoms during its path out of the molecule. A discussion of other mechanisms which can lead to our results will also be given. For instance, a high probability of double Auger decay in the symmetric molecules may explain our observations. Previously,[1] small variations ($\lesssim 10\%$) in Auger emission cross section, σ_A, for molecular targets were ascribed to modifications in the Coulomb ionization cross section due to specific molecular environments. We will show that neither ionization–cross-section changes nor variations in fluorescence yields can account for our observations of variations in σ_A for sulfur *LMM* decay from H_2S, SO_2, and SF_6 targets as well as carbon *KLL* emission from CH_4, CCl_4, and CF_4.

These measurements were performed using a Van de Graaff accelerator, a differentially pumped gas cell, a parallel-plate electron analyzer, and an x-ray proportional counter. The accelerator produced proton beams at energies of 0.5, 1.0, and 1.5 MeV that were directed through a 75-mm-diam gas cell and stopped in a Faraday cup. Auger electrons were energy selected by the parallel-plate analyzer and detected by an electron multiplier. Auger yields were measured for all targets at a lab angle of $\theta_L = 160°$. For SF_6 the yield was also measured at $\theta_L = 90°$ where the yield the same as at $\theta_L = 160°$ thus indicating isotropic emission. After correction for the electron-analyzer transmission function,[2] Auger cross sections were determined by comparing sulfur *LMM* and carbon *KLL* yields to a measurement of Ar *LMM* yield, for which the cross section is known.[3] The response of the e^- analyzer from 0 to 500 eV was tested by measuring $p + H_2$ "ejected"-electron energy spectra and comparing to those of Toburen and Wilson.[4] Exact agreement was observed for e^- energies above 10 eV which is adequate for the phenomenon discussed here. Sulfur *L* x-ray measurements were performed by positioning a proportional counter such that it viewed the same interaction region observed by the electron analyzer. All Auger electron experiments were performed with a gas-cell pressure of 1.0 or 2.0×10^{-3} Torr, a pressure region wherein the Auger yields were observed to be *linearly* dependent on pressure. X-ray measurements were performed with a gas-cell pressure of 25×10^{-3} Torr and all yields normalized to that of the Ar *L* x rays, for which the cross section is known.[3]

The principal results of these measurements are shown in Figs. 1(a), 1(b), and Table I. Figure 1(a) illustrates sulfur *LMM* Auger spectra for SF_6 and SO_2, which have not been corrected for the E^{-1} (E is analyzed electron energy) analyz-

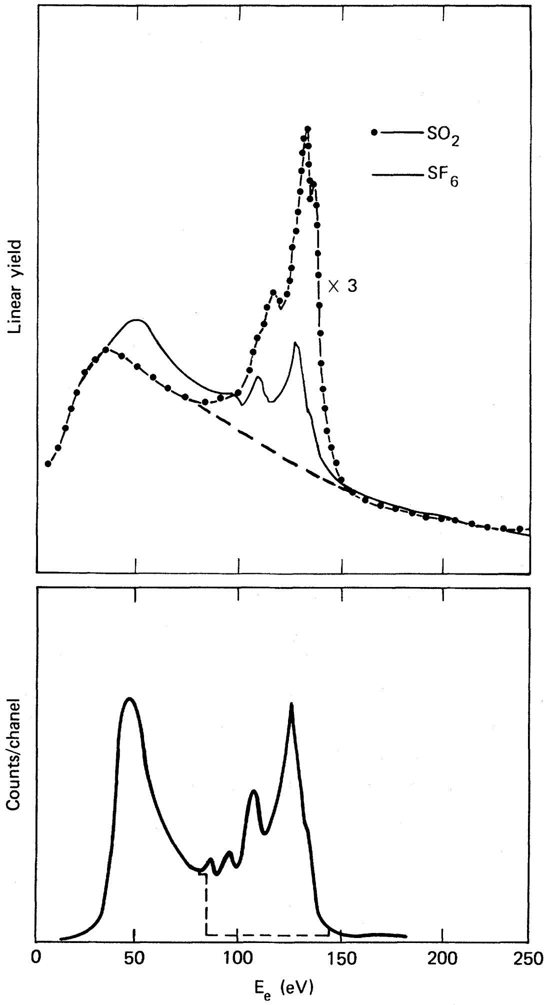

FIG. 1. (a) Sulfur *LMM* Auger spectra from 1.5-MeV $H^+ \rightarrow SO_2$ and SF_6 collisions, $\theta_L = 160°$. Spectra were normalized in intensity at high and low energies; then the SO_2 spectrum with dashed line instead of peak was subtracted from the SF_6. The spectra are not corrected for analyzer transmission nor has any background been subtracted prior to plotting. (b) SF_6 spectrum with background subtracted and corrected for analyzer transmission. Dashed line indicates region integrated for characteristic Auger yield.

er transmission function. The Auger yields for all cases but SF_6 were obtained by fitting a linear background to the regions on either side of the peak and subtracting it from the total peak yield. For the case of SF_6 another fitting technique proved necessary because of the presence of a broad "bump" at ~50 eV. The SO_2 spectrum was normalized to that of the SF_6 at high and low electron energies. Next, the dashed-line background function was substituted in the SO_2 peak region. Then the resulting background shape was subtracted from the SF_6 spectrum. Figure 1(b) demonstrates the resultant spectrum which has also been corrected for analyzer transmission. The spectrum consists of a broad bump centered at about 50 eV, the characteristic sulfur *LMM* lines centered at about 129 eV, and some type of smooth tail merging the broad bump to the characteristic lines. Although the bump was also observed when bombarding a CF_4 target, it is too energetic to be assigned to any known autoionizing transitions.[5] However, it is interesting to note that integration of the electron yield in the bump region plus the characteristic region recovers all the missing electron yield!

Table I illustrates the cross sections σ_A and σ_X for all the Auger and x-ray measurements. The most remarkable feature is the variation with different molecular targets. With the use of sulfur as an example, the Auger yield is approximately halved in going from the angular molecules H_2S and SO_2 to the octahedral SF_6 molecule. To a lesser extent we see this same effect in the tetrahedral carbon molecules—again with the lowest yield being observed for the molecules containing the highest-Z bonding partners. In the sulfur molecules, the L x-ray yield increased (the Auger yield decreased) for the SF_6 molecule, thus indicating a significant change in fluorescence yield, ω. We measured $\omega(H_2S)$ to be 4.1×10^{-4} compared to the theoretical value of 2.9×10^{-4} from Bambynak *et al.*[7] However, the probability for x-ray emission is a thousand times smaller than for Auger emission, thus the changes in Auger yields in Table I cannot be ascribed to increased x-ray yields.

Using the binary-encounter formulation for Coulomb ionization,[8] the vacancy cross section σ_V is proportional to the quantity G/U_B^2, where U_B is the binding energy of the electron to be ionized and G is the "universal" function which depends upon the ratio of ion velocity to the orbital velocity of the electron. Changes in G for our cases are negligible so that σ_V essentially scales as U_B^{-2} for fixed ion velocity. The column in the table labeled σ_V for theoretical vacancy production illustrates that the observed variations cannot be ascribed to changes in the sulfur $2p$ or carbon $1s$ binding energies.[5]

Because neither fluorescence yield variations nor the effect of shifts in inner-shell binding energy could explain the loss in Auger yield for SF_6, CCl_4, and CF_4 molecules, we developed a simple empirical model. Consider that Auger electrons from the "core" sulfur or carbon atoms are in-

TABLE I. 1.5-MeV-proton–induced sulfur L and carbon K Auger and x-ray production cross sections. Values measured for proton bombarding energies of 0.5 and 1.0 MeV did not differ appreciably relative to σ_A and σ_x of Ar L-vacancy production as published in Ref. 3. The uncertainty quoted for all measurements is relative to the Ar σ_x, σ_A determination. $\sigma_x = 1.5 \times 10^{-21}$ cm^2 (± 25%); $\sigma_A = 3.2 \times 15^{-18}$ cm^2 (± 25%).

Target	σ_A (10^{-18} cm^2)	σ_x (10^{-21} cm^2)	U_B[a] (eV)	σ_V ($\sim U_B^{-2}$)	1-$P_{\rm inel}$
H_2S	4.6 ± 0.2	1.7 ± 0.2	2p: 170.6	4.6[b]	0.96
SO_2	4.6 ± 0.2	1.7 ± 0.2	174.8	4.9	0.90
SF_6	2.2 ± 0.2[c]	2.4 ± 0.2	180.8	4.1	0.83
CH_4	1.08 ± 0.06	⋯	1s: 290.7	1.1[b]	0.92
CCl_4	0.73 ± 0.09	⋯	296.2	1.1	0.82
CF_4	0.89 ± 0.10	⋯	301.8	1.1	0.87

[a] From Siegbahn *et al.*, Ref. 5.

[b] Normalized to corresponding σ_A.

[c] We measure $\sigma_A(SF_6) = 2.6 \times 10^{-18}$ cm^2 for 1.0-MeV H^+ bombardment as compared to that of Toburen *et al.*, Ref. 6, $\sigma_A(SF_6) = 2.7 \pm 0.9 \times 10^{-18}$ cm^2.

elastically scattered during transit through the surrounding fluorine or chlorine atoms. We argue that the Auger electrons originate from within the mean radius of the molecule even though valence electrons are involved in the transition. Using the SF_6 as an example, the nature of the ligand bonding requires that the valence electron spend at least half of its orbit time near the sulfur atom. Considering that six electrons are involved implies that the average valence-electron density is quite high near the sulfur atom and therefore inside the mean radius of the molecule. Obviously, then, the maximum probability for an Auger transition occurs at the point of greatest electron density and spatial overlap with the sulfur $2p$ (initial state) wave function. This simple picture supports the idea that some fraction of the Auger electrons could then scatter off electrons near the fluorine atoms during their transit out of molecule. For this model we require the energy loss to be such that a "smearing" into the background (or perhaps into the 50-eV mystery peak) occurs for characteristic-energy Auger electrons. A simple quantitative estimate of the magnitude of this effect can be obtained since total inelastic scattering cross sections $\sigma_{\rm inel}$ for 129-eV (sulfur LMM) and 270-eV (carbon KLL) electrons on the molecules H_2, O_2, Cl_2 (used Ar value), and SF_6 are known.[9] Assuming constant dependence of the scattering probability on impact parameter, we can formulate a geometrical expression for the probability that an inelastic scattering event takes place,

$$P_{\rm inel} = \frac{\Delta\Omega_{\rm scat}}{4\pi} \simeq \tfrac{1}{2}\left\{1 - \cos\left[\tan^{-1}\frac{(\sigma_{\rm inel}/\pi)^{1/2}}{d_m}\right]\right\}N,$$

where N is the number of electronegative atoms and d_m is the bond length from the core atom to the electronegative atom. We have tabulated the transmission quantity $(1 - P_{\rm inel})$ in the last column of Table I for comparison to experiment. The transmission probability for Auger emission from all these molecules is observed to vary in qualitative agreement with experimental findings. However, there are substantial discrepancies in the absolute comparison which are due to our unsophisticated calculation of $P_{\rm inel}$.

A straightforward test of our inelastic scattering hypothesis can be performed by means of photoabsorption experiments. Specifically, a measurement of the yield of equivalent energy photoelectrons from the core atoms of these special molecules should also exhibit variations with molecular environment.

There exists another phenomenon which can affect the probability of electron emission from inside nearly symmetric molecules. Dehmer[10] has described a mechanism known as resonant absorption or potential-barrier scattering wherein low-energy photoelectrons get trapped or lose some energy in emerging from molecules like SF_6. However, measurements of this effect show that it is usually important for very low-energy electrons (~ 10 eV or less).[6] One could also argue that the electron ejected by the proton in these collisions could get trapped in the potential well created by the barrier. In this case Auger decay could still easily occur although the transition energies would be shifted downward (~ 5 eV) due to the presence of an extra electron in the initial and final states. At any rate this effect is not expected to alter drastically the Auger rates or to increase the barrier height such that Auger electron decay is inhibited.

Another phenomenon which can contribute to loss of characteristic Auger electrons is the double Auger process[11] which has been studied for noble-gas atoms. In double Auger decay an outer-shell electron fills the inner-shell vacancy while *two* other outer-shell electrons are simultaneously excited into two states. One of these states can still be a discrete (higher n) state whereas the other will be in the continuum. Measured[12] discrete double Auger transitions are shifted down in energy relative to the single Auger lines; so they could be responsible for the tail between the bump and the characteristic sulfur LMM lines. Moreover, double Auger decay to the continuum could result in a continuous distribution of electron energies which could possibly produce the bump. Measurements of the relative rate for the double Auger process indicate that it can be as large as 30% (see review from Åberg[13]) of the normal rate, when the outer-shell Auger decay of a large noble-gas atom such as Kr is involved. In fact, a dependence of the double Auger rate on Auger electron kinetic energy was observed[14]—higher rates for lower kinetic energy. Perhaps in our large SF_6, CF_4 and CCl_4 molecules this effect could also be significant even though the sulfur $2p$ and carbon $1s$ shells have a larger binding energy (thus resulting in higher Auger-electron energies) than krypton. One should not assign great significance to this energy dependence since Carlson and Krause[15] have concluded that electron-electron correlation effects are necessary to describe the rates for the double Auger process. These correlations would be sensitive to the varying orbital electron structure in our molecules. Unfortunately, there is at present no theoretical treatment of the probability of the double Auger process for molecular states.

Finally, the results of our measurements have important ramifications for atomic collisions studies since they demonstrate that *atomic* vacancy production cross sections cannot necessarily be deduced from Auger electron measurements which have been performed using molecular targets.

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