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Chemical effects in the *K* x-ray yield of sulfur

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We have observed a chemical-environment effect on the total *K* x-ray yield of sulfur in SF_6, SO_2, and H_2S. The yield from SF_6 is 16% higher than the yield from H_2S, whereas the yield from SO_2 is, within error, the same as H_2S. Variation in the fluorescence yield for the different molecules is considered to be the most probable cause of the effect.

I. INTRODUCTION

The first direct observation of a chemical-environment effect on the *K* x-ray yield was reported by Harrison, Tawara, and DeHeer[1] for electron bombardment of carbon-bearing molecules. They found a decrease in the *K* x-ray rate of as much as 35% between CO and CH_4. They suggested that the cause of the observed differences in rate was a variation in fluorescence yield which depended on the molecular environment of the carbon atom. Calculations by Manne[2] of the *K* x-ray spectrum for carbon in various molecules suggested significant variations which might be expected to show up as a different total rate, but no specific rate calculations have as yet been done. The carbon molecules have also recently been studied by Bissinger *et al.*[3] using protons as the bombarding particle. They observe behavior of the *K* rate which is generally in agreement with those of Harrison *et al.*, although they find a difference between CO and CH_4 of only 16%. They suggest that the *K* x-ray rate is correlated with the number of valence electrons with *p* character available to fill a *K* vacancy. They have also used this explanation to describe data on the *K* rates of oxygen and fluorine.[4] Data on molecular-environment effects have also come from *K* Auger rate measurements on fluorine where the effects, if any, are small.[5]

The purpose of the present experiment was to look for chemical effects on the *K* x-ray yield of sulfur by electron bombardment of free gas molecules: H_2S, SO_2, and SF_6. Chemical effects have been observed by Watson *et al.*[6] in the $K\alpha$ satellite spectrum from heavy-ion bombardment of sulfur molecules. A chemical effect on the total *K* x-ray rate might be expected to be much smaller than that seen in carbon because of the increased *K* shell binding energy of sulfur. However, it was felt that increased sensitivity could be obtained by simultaneously observing both the *K* x ray and the bremsstrahlung produced in the electron bombardment of the gas, as discussed below.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in this experiment has been described previously.[7] Essentially it consists of a tungsten-filament electron gun which produces an electron beam that crosses a gas beam introduced into the scattering chamber through a capillary array. The photons produced at 90° to the incident electron beam are detected in a Si(Li) detector. The ambient pressure in the scattering chamber is about 10^{-4} torr when the target gas is flowing. The pressure in the interaction region is larger than the ambient pressure and has not been directly measured. As discussed below, neither the total incident electron charge nor the gas pressure (target thickness) figure in the analysis of the data. The detector efficiency has been well modeled from 1.5 to 15 keV; but, as we shall see below, uncertainty in the detector efficiency does not affect the main conclusions of this experiment.

A typical photon energy spectrum is shown in Fig. 1. The electron bombarding energy was 10 keV and the target gas was H_2S. The spectrum consists of a bremsstrahlung continuum extending up to the kinematic "end

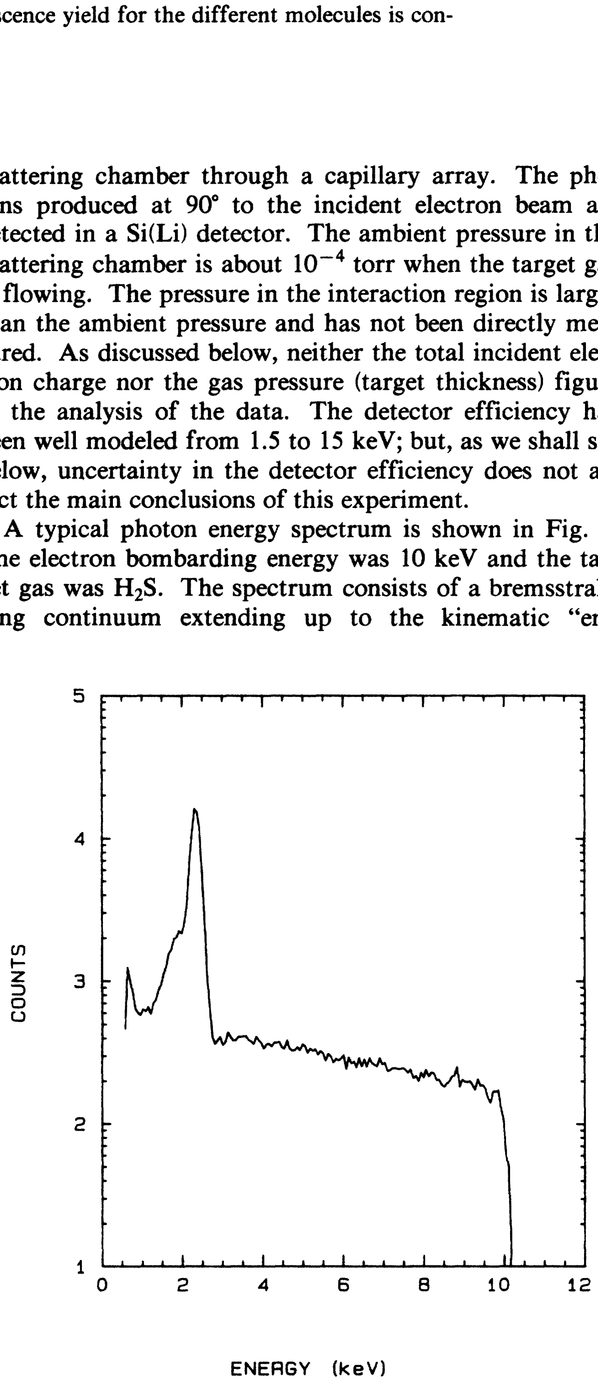

FIG. 1. The log of the number of counts versus radiated photon energy for 10-keV electrons on H_2S. The end point of the bremsstrahlung continuum is at 10 keV. The sulfur *K* x-ray peak is at 2.3 keV. Detector noise is below about 1 keV.

point" equal to the incident electron energy and the characteristic K x ray of sulfur at about 2.3 keV. X rays below about 1.0 keV do not reach the detector, hence, we do not observe the K x rays of fluorine or oxygen from the target. The increase in counts below 1 keV is due to detector noise. Because of the detector efficiency, most of the counts observed below about 2 keV are due to the response of the detector to the intense K x-ray peak. The $K\alpha$ and $K\beta$ peaks are unresolved.

Background runs were made with the target gas flow off, and with the electron beam off. Both were found to be negligible for the targets considered here, and no background subtraction was considered necessary.

To determine the K x-ray yield, we sum the K x-ray peak and subtract a bremsstrahlung background determined by averaging the counts before and after the peak. The value of the sum is insensitive to the width chosen within reasonable limits. However, the uncertainty introduced in the number of K x rays from this background subtraction remains the largest experimental uncertainty in the experiment. The number of bremsstrahlung counts over a selected photon energy range is determined by summing the data over the appropriate channels. Because both the K ionization and the bremsstrahlung process depend in the same way on the number of incident electrons, the target gas thickness, and the detector solid angle, the ratio of the K x-ray peak to the bremsstrahlung over any photon energy region is independent of these factors. Thus the experiment is capable of increased sensitivity in determining the x-ray yield from different target gases.

III. RESULTS AND DISCUSSION

The results for the ratio of the number of K x rays to bremsstrahlung for 8- to 15-keV electrons on H_2S, SO_2, and SF_6 are plotted in Fig. 2 for a bremsstrahlung photon energy range from 3 to 7 keV. The ratios shown have been corrected for the difference in efficiency of the detector for the K x ray at 2.3 keV compared to the energy range from 3 to 7 keV and thus are absolute ratios. The relative efficiency is a scale factor and is known to an accuracy of about 3%.

If we assume that the bremsstrahlung cross section is known from theoretical calculations, then the absolute K x-ray yield can be determined. We have previously used this approach to measure the K-shell ionization cross section of argon and the L-shell ionization cross sections of krypton and xenon.[8] However, at this point, it is interesting to note that the ratios increase with energy. To understand this simple behavior we need first to compute the bremsstrahlung cross section. The atomic-field bremsstrahlung cross sections have been tabulated.[9] We have used the same interpolation procedure to obtain atomic-field bremsstrahlung cross sections for the atoms of sulfur, fluorine, oxygen, and hydrogen for the bombarding energies and radiated photon energies of interest. The bremsstrahlung cross section for the molecule is computed by assuming additivity of the atomic-field cross sections for the atoms comprising the molecules. Recently, we have presented evidence for the validity of the additivity assumption in this energy range for the sulfur-bearing gases, as well as for various hydrocarbon gases.[7,10,11] Of relevance here is the observation that the scaled cross section $k\beta^2/Z^2(d\sigma/d\Omega dk)$ is essentially constant over the radiated photon energy range from 3 to 7 keV. Here, $d\sigma/d\Omega dk$ is the bremsstrahlung cross-section differential in photon energy and angle, β^2 is the square of the incident electron's velocity relative to the speed of light, and Z is the atomic number of the atom. Of course, the scaled cross section varies from one atom to another, but if we assume additivity for the molecular cross section, then the measured bremsstrahlung rate is essentially proportional to β^{-2}.

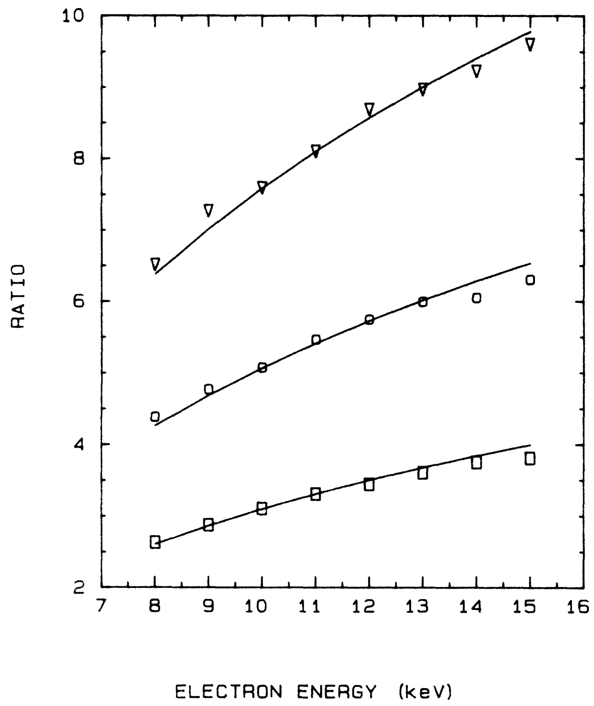

FIG. 2. The ratio of the number of sulfur K x rays to the bremsstrahlung radiated between 3 and 7 keV for H_2S (triangles), SO_2 (circles), and SF_6 (squares) versus incident electron energy. The solid lines are $\ln(\beta^2/2I)$ normalized to the data at 10 keV.

The K x-ray yield is the product of the K ionization cross section, σ_K, and the fluorescent yield, w_K. While the details of the behavior of the K ionization cross section of sulfur are yet to be determined, experience with other atoms in this energy range suggest that the ionization cross section scales with β^2/I, where I is the ionization potential. The simple Bethe approximation gives $\sigma_K = \ln(\beta^2/2I)/\beta^2$. Thus the ratio of the K x-ray yield to the bremsstrahlung rate should behave as $\ln(\beta^2/2I)$. This energy dependence is shown as the solid line in Fig. 2, scaled in each case to the experimental value at 10 keV. Clearly the behavior of the data is consistent with this simple analysis.

In order to obtain the relative K x-ray yield for the different target gases, we have taken the ratio of the ratios shown in Fig. 2 for pairs of molecules. The results are given in Table I. The ratios are independent of electron bombarding energy and have been averaged. The expected ratios are simply the ratios of the molecular bremsstrah-

TABLE I. The ratio, for different molecules, of the ratio of the number of K x rays to the bremsstrahlung produced from 3 to 7 keV versus incident electron energy. The theory assumes the K x-ray rates are equal and exhibits the differences in the bremsstrahlung rate for each molecule.

Electron energy (keV)	$I(SF_6)/I(H_2S)$	$I(SF_6)/I(SO_2)$	$I(SO_2)/I(H_2S)$
8	0.4032	0.5992	0.6729
9	0.3943	0.6015	0.6556
10	0.4083	0.6110	0.6682
11	0.4075	0.6044	0.6742
12	0.3955	0.5988	0.6604
13	0.4012	0.6009	0.6678
14	0.4057	0.6191	0.6552
15	0.3962	0.6039	0.6560
Average	0.4014±0.0054	0.6049±0.0065	0.6638±0.0074
Theory	0.3460±0.0030	0.5136±0.0055	0.6736±0.0067
Expt./Theory	1.160 ±0.018	1.178 ±0.018	0.985 ±0.015

lung cross sections which are also independent of energy and have been averaged. This theory assumes that the ratio of K x-ray yield from the different molecules is one. The difference between experiment and theory for SF_6 to H_2S is (16.0±1.8)%, for SF_6 to SO_2 is (17.8±1.8)%, and for SO_2 to H_2S is (−1.5±1.5)%. Hence, the conclusion is that the K x-ray yield from sulfur in SF_6 is 16% higher than from sulfur in H_2S, and that the rate from sulfur in SO_2 is, within error, the same as that from H_2S.

We have considered three possible explanations for this effect. First, the K ionization cross section could be higher for sulfur in SF_6 than for sulfur in H_2S or SO_2. The change in ionization potential for the sulfur K shell due to chemical shift is much too small, however, to explain the observed effect.

Second, the bremsstrahlung rate could be incorrectly calculated for the atoms, or there could be some nonadditive effect on the bremsstrahlung rate which leads to a lower rate from SF_6 relative to H_2S and SO_2. Using the measured ratios, we can determine the difference in the scaled atomic-field bremsstrahlung cross section that would be required to explain the effect. If we assume that oxygen is correct, then we would require sulfur to be about 1% less than oxygen, and fluorine to be about 22% less than oxygen. While the theoretical atomic-field bremsstrahlung cross sections are not accurate enough to rule out a 1% effect, it is very implausible that fluorine would differ from oxygen by 22% when it differs by only one in Z.

Although absolute cross sections are not available for the targets or energies considered here, there are absolute data for 50 keV and above for thin-film targets with atomic numbers ranging from carbon to uranium[12–14] which show good agreement with theory at about the 20% level of accuracy. The consistency of the data at higher energies, over the whole range of atomic number, gives us some confidence in the accuracy of the theory at lower bombarding energy. However, it should be recognized that until absolute cross-section data are available for gas targets in the 10-keV energy range, we cannot rule out a discrepancy in the bremsstrahlung rate as an explanation of this effect.

Third, the fluorescent yield could depend on the molecular environment. This has been invoked by Harrison *et al.*[1] to explain the effects observed in carbon; we believe it is the most plausible explanation for the effect observed here. Although no detailed theory is available, a variation in fluorescent yield could arise in several ways. Direct multiple ionization or multiple ionization resulting from shake-up or shake-off processes could lead to a variation. If the rates for these processes were to depend significantly upon the molecule, then the resulting difference in average vacancy distribution of the molecule could perhaps lead to the observed effect.

An experiment to study the sulfur K x-ray region in high resolution with a crystal spectrometer using helium bombardment of these gases is underway. X-ray fluorescence of the gases in a static gas cell using the Si(Li) detector is also planned. These experiments should further help decide between the accuracy of the bremsstrahlung normalization and variation in fluorescence yield as the cause of the effect.

IV. CONCLUSIONS

To conclude, we have observed an increase in the K x-ray yield of sulfur in SF_6 compared to SO_2 and H_2S of 16–18%. The SO_2 and H_2S yields are the same within errors. The data behave otherwise as would be expected from consideration of the bremsstrahlung and ionization cross-section theory. While we cannot rule out a discrepancy in the absolute bremsstrahlung rate, we consider a variation in fluorescence yield with molecular environment to be the most probable cause of the observed effect.

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