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THE RELATIVE FLUORESCENT EFFICIENCY OF
SODIUM SALICYLATE BETWEEN 90 AND 800 eV

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ABSTRACT

The relative fluorescent quantum efficiency of sodium salicylate was measured between 90 and 800 eV (138 - 15 Å) by the use of synchrotron radiation. A general increase in efficiency was observed in this spectral range except for abrupt decreases in efficiency at the carbon and oxygen K-edges. Beyond the oxygen K-edge (532 eV) the efficiency increased linearly with the incident photon energy to the limit of the present observations.

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INTRODUCTION

When radiant energy greater than 3.5 eV is incident on sodium salicylate it is partially converted to fluorescent radiation whose spectral distribution, lying between 3500 and 5500 Å, has been found to be independent of the exciting wavelength.¹ Previous investigations have shown that the quantum efficiency, η , of the salicylate, defined as the number of fluorescent photons produced per incident exciting photon, is constant over an extended wavelength range (100 - 3500 Å).²⁻⁶ As a result sodium salicylate in conjunction with conventional photomultipliers has been widely used as a sensitive detector in the vacuum ultraviolet (VUV) spectral region. Krokowski,⁷ however, using x-rays of energy greater than 12 keV, has shown that here the quantum efficiency is no longer constant but increases linearly as a function of energy with a conversion factor, defined as the ratio of fluorescent to absorbed energy, of 0.04. By extrapolation of his results Krokowski suggested that a change from an energy independent to an energy dependent efficiency would occur at about 83 eV, assuming the efficiency to be unity in the energy independent region. This transition was not observed by Samson and Haddad⁵ who investigated the relative fluorescent efficiency of sodium salicylate between 20 and 107 eV and found it constant to within $\pm 8\%$. However, subsequent unpublished results from this laboratory using a different technique have indicated a possible increase in efficiency for photon energies greater than 50 eV. In addition Lindle *et al*⁸ report an increase in the quantum efficiency of about a factor of 2 between 80 and 270 eV.

Increasingly, synchrotron radiation in the VUV and soft x-ray regions is being used to study atomic and molecular processes, and in this range sodium

salicylate is a popular detector. When it is used to measure the relative photon intensity as a function of wavelength it is important that the true relative variation of the sodium salicylate quantum efficiency be known in order to interpret accurately the data taken.

With this in mind an experiment was designed to measure the relative fluorescent efficiency of sodium salicylate over the energy range provided by the monochromator of beam line U14 at the Brookhaven National Synchrotron Light Source. We wished particularly to identify the wavelength region where the transition from an energy dependent to an energy independent efficiency occurs, and, since both carbon and oxygen form the major components of sodium salicylate ($\text{NaC}_7\text{H}_5\text{O}_3$), to observe the effect on the efficiency of the carbon and oxygen K-shell absorption.

EXPERIMENTAL APPROACH

The fluorescent efficiency of sodium salicylate η is defined as,

$$\eta = I_f/I_o \quad , \quad (1)$$

where I_f is the number of fluorescent photons/s and I_o is the number of incident photons/s. I_f is measured with a sodium salicylate/photomultiplier combination whose output I_{PM} is proportional to I_f .

The intensity of the incident radiation was determined by measuring the ionization produced as it passed through a low pressure noble gas target. Because every absorbed photon produces an ion whether singly or multiply charged, the number of ions N collected over a path length l is given by,

$$N = I_o \sigma n l \quad , \quad (2)$$

where n is the number density of the gas and σ is the absorption cross section. From Eqs. (1) and (2) it can be seen that for constant $n l$ we obtain

$$\eta \propto I_{PM} \sigma / N \quad . \quad (3)$$

I_{PM} and N are readily measured quantities and σ is well known for the rare gases with an accuracy of better than $\pm 10\%$.⁹ However, the efficiency of the ion detector will be somewhat different for the various charged states of the ions. This effect can be minimized by using the detector in the counting mode.

Figure 1 shows a schematic diagram of the apparatus used in the experiment. Radiation from the grazing incidence monochromator was directed through two low conductance canals D_1 and D_2 , which provided differential pumping to maintain the high vacuum conditions necessary for the monochromator and beam line. The radiation passed through the collision region C and was then incident on the salicylate screen S where the fluorescent radiation was detected by the photomultiplier tube PM . The signal I_{PM} was measured with a picoammeter. In traversing the collision region the photon beam intersected the collimated gas flow from the capillary tube L . The gas pressure in the reservoir R was maintained at a constant pressure, to within approximately 0.2%, by the servo-needle valve S controlled by the capacitance manometer B . This ensured that that under equilibrium conditions the product nL remained constant. Ions formed in the collision region were extracted with high efficiency by the extraction and lens system EL and were recorded by an electron multiplier M used in the single particle counting mode.

Data acquisition and monochromator control was handled by the computer system provided by the operating staff of Beam line U14. Photon energies from < 20 eV to more than 800 eV were provided by the 4 ranges of the monochromator; target gases helium, neon, and argon were used. For each monochromator range the photomultiplier current and ion count rates were recorded at a fixed gas pressure for a series of energies covering the spectral range investigated. Two salicylate coatings were investigated, each being applied to the glass

window S by spraying a saturated solution of sodium salicylate in methanol onto the warmed surface. Several applications of light coats were used to build up a surface with a uniform opaque appearance. No estimate was made of the actual surface density.

Prior to measurements of the salicylate efficiency the system, which was pumped by three Balzer turbo molecular pumps, was baked. On cooling, the base pressures in the differential, collision, and ion detector regions were 2.6×10^{-8} , $< 1.0 \times 10^{-6}$, and 1.5×10^{-7} torr, respectively. With typical running conditions of 0.3 torr in the reservoir chamber the target chamber background pressure rose to 6×10^{-6} torr and the pressure in the differential region rose to 3×10^{-8} torr. No increase in the monochromator pressure was apparent. From the measurements of I_{PM} and N the relative variation of the sodium salicylate efficiency could be determined as a function of energy.

ANALYSIS OF THE RESULTS

A major difficulty in analyzing data taken with a continuum, as opposed to a discrete line source, is separating true signal from that arising from contamination due to higher order and scattered radiation. An estimate of the long wavelength scattered radiation was made as follows. Valve V contained a sapphire window opaque to radiation with $\lambda < 1410 \text{ \AA}$. With this valve closed the signal from the photomultiplier was recorded as a function of energy for each of the four monochromator ranges. These scattered radiation spectra, when normalized to unit electron current circulating in the storage ring, could be used to estimate the background scattered signal at the photomultiplier caused by radiation with $\lambda > 1410 \text{ \AA}$, provided the storage ring current during the measurement was known. These currents were recorded before and after every energy scan on each range. The contribution to the signal caused by the long

wavelength scattered radiation and the photomultiplier dark current was subtracted from all photomultiplier signals. No allowance could be made for scattered radiation with wavelength greater than 1410 Å or for any ion signal arising from it.

Figure 2(a) shows the data taken on range 2 between 80 and 380 eV. The continuous curve shows the output from the photomultiplier (with the dark current and the estimated long wavelength scattered contribution subtracted). The chain curve shows the Ar ion count rate. Figure 2(b) shows the uncorrected relative efficiency of the sodium salicylate response calculated using Eq. (3). The following features in the Figures should be noted.

(a) The increase in the ion count rate between 240 and 260 eV in Fig. 2a corresponds to increased absorption at the argon $L_{2,3}$ edge. A similar increase is observed at approximately 120 eV caused by second order $L_{2,3}$ absorption. Discontinuities at these energies are also observed in the sodium salicylate efficiency curve. With an exact knowledge of the argon absorption cross section, the true background signals for both the photomultiplier current and the ion signal, and an exact calibration of the energy scale these discontinuities would not arise. Since none of these conditions apply such structure will occur where sharp resonances in the cross section exists. In regions where the cross section is smoothly varying the effect of these uncertainties is minimized.

(b) The rapid decrease in the photomultiplier signal above 280 eV corresponds to the absorption of the incident radiation by carbon in sodium salicylate at the carbon K-edge (288 eV). This is reflected in the sharp decrease in the sodium salicylate efficiency shown in Fig. 2(b).

The structure in the photomultiplier signal at approximately 140 eV is caused by second order carbon K edge absorption. Similar structure at ~ 95 eV shows third order contamination. All the structure observed in the sodium salicylate response curve between 80 and 160 eV is a result of higher order

contamination. From the nature of the monochromator design^{10,11} each of its ranges had limits within which reflection filtering had theoretically reduced higher order contamination to zero. However, while in theory photon energies from 20 to 800 eV could be provided free of higher orders, it was found in practice that the two lowest energy monochromator ranges, 3 and 4, had either significant higher order contamination, or insufficient radiant output over the wavelength range of interest, so that the acquisition of reliable data was precluded. In order to obtain information on the variation of the salicylate efficiency over as wide an energy range as possible an attempt was made to remove the effects of higher order contamination from the data taken with the range 2 mirror at energies below 150 eV. Figure 3 shows a detailed plot of the photomultiplier output between 80 and 160 eV; the effect of the 2nd order carbon K edge at 140 eV is clearly seen. Beneath the measured curve (full line) is an estimate of the true variation of the first order radiation (chain curve). By subtraction the contribution due to second order radiation at any energy E could be found and expressed as a percentage of the radiation at energy 2E. This percentage then gave the contribution of the ion signal at energy E caused by ions formed by radiation of energy 2 E, and this contribution could be subtracted from the total ion count rate. The corrected photomultiplier currents and ion count rates could then be used to calculate corrected salicylate efficiencies. A similar procedure was used to correct the data taken with the range 1 mirror; the correction was only appreciable between 400 and 450 eV.

DISCUSSION

Figure 4 shows a plot of the corrected relative fluorescent quantum efficiency of sodium salicylate as a function of the incident photon energy from 90 to 800 eV. The solid data points represent the results taken with a single salicylate coating with argon as the target gas. The open data points

represent the results taken with neon as the target gas. The same overall relative variation was shown by a second coating and other target gases. The difference in the Ar and Ne data between 90 and 120 eV demonstrates the problem of correcting for second and higher order spectra in this region.

The results in Fig. 4 were normalized to the data of Krokowski in the region above 550 eV where it was assumed that 4% of the incident energy was converted to fluorescent photons as he reported. The incident photon energy E_{inc} and mean fluorescent energy E_f are then related by the expression

$$\frac{N E_f}{E_{inc}} = 0.04 \quad , \quad (4)$$

where N is the number of fluorescent photons emitted. The scale of the ordinate was adjusted so that a least square fit to our data points, passing through the origin, showed the appropriate slope of .0144 where we have assumed $E_f = 2.78$ eV. The dashed horizontal line represents a constant quantum efficiency of unity and intersects the extrapolated slope at 70 eV. However, the absolute value of the constant quantum efficiency portion has been variously reported in the literature to be in the range 0.5 to 1.0.¹²⁻¹⁷ Thus, the ordinate scale represents a maximum efficiency for our present results as shown in Fig. 4. This is because by normalizing the constant quantum efficiency to the tail of the Ar or Ne data would require lowering the entire curve to allow the constant efficiency portion to be less than or equal to unity.

The distinctive features above 160 eV are independent of the absolute ordinate scale. Thus the step increase in the response preceding the fall at the carbon absorption edge, the less steep increase preceding the discontinuity at the oxygen edge followed by the uniform increase to 800 eV shows the relative variation of the quantum efficiency of sodium salicylate as measured in the experiment. There is insufficient data to say whether the apparent change in slope at 400 eV is significant. Figure 5 shows a detailed plot of the

salicylate efficiency in the region of the carbon K edge. The point of inflection at ~ 290 eV was a repeatable feature independent of target gas for both salicylate coatings. Norman¹⁸ in his review of surface EXAFS and XANES has shown that absorption spectra in the neighborhood of absorption edges are rich in structure which may frequently be associated with specific interatomic bonds. No investigation of sodium salicylate has been reported but it seems not unreasonable that the structure in the efficiency curve arises from processes similar to those revealed by EXAFS.

The present results disagree with Lindles' reported measurement of an increase of a factor 2 between 80 and 270 eV.⁸ We find an increase of 3.6 between 150 and 270 eV, a region in which we have applied no corrections to the data.

It is unfortunate that data taken with the low energy mirrors could not be adequately analyzed to provide reliable information on the interesting transition region from 50 to 150 eV. It is hoped to study this range in more detail in subsequent experiments.

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FIGURE CAPTIONS

Fig. 1. Schematic diagram of the apparatus, (a) seen from the side and (b) viewed end on.

Fig. 2. (a) Photomultiplier signal (full curve) and ion count rate (chain curve) as a function of photon energy. (b) Salicylate efficiency as calculated using Eq. (3) from the data shown in Fig. 2a.

Fig. 3. Photomultiplier output (full curve) between 80 and 160 eV and the estimated true first order signal (chain curve) used to correct for second order contamination (see text).

Fig. 4. The variation of sodium salicylate quantum efficiency as a function of photon energy. The full circles are data taken with Argon as the target gas, the open circles were taken with neon. Both the argon and neon data are corrected for higher order contamination below 160 eV; the horizontal dashed line represents the unit efficiency of previous measurements. The full line represents the 4% energy conversion factor predicted by Krokowski. The positions of the carbon and oxygen K absorption edges are marked.

Fig. 5. The sodium salicylate efficiency as a function of photon energy in the region of the carbon K edge. The line is drawn as a guide to the eye only.









