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Increasing Quantum Yield of Sodium Salicylate Above 80 eV Photon Energy: Implications for Photoemission Cross Sections

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The quantum yield of the visible scintillator sodium salicylate is found to increase by approximately a factor of two in the photon-energy range 80–270 eV. Because of its use as a photon-flux monitor in recent gas-phase photoelectron spectroscopy measurements, previously reported partial cross sections for Hg (4f, 5p, and 5d subshells) and CH$_3$I (I 4d subshell) in this energy range are corrected, and new values are reported. For Hg, the correction brings the experimental data into better overall agreement with theory. However, considerable uncertainty remains in the absolute scale derived from previous Hg photoabsorption measurements, and no single rescaling of the subshell cross sections could simultaneously bring all three into agreement with available theoretical calculations.
I. Introduction

The determination of photoemission cross sections using synchrotron radiation in the photon-energy range in which core-level electrons can be ionized (~50 eV and higher) requires a reliable photon-flux monitor. For our measurements, we chose the visible scintillator sodium salicylate, because it was reported to have a constant quantum yield of optical photons relative to incident photons to within 5%, for incident photon energies up to 107 eV.\(^1\) Based on the assumption that this quantum yield remains constant at higher photon energies, we recently reported partial cross-section results up to 270 eV for the Hg 4f, 5p, and 5d subshells,\(^2\) and the methyl iodide I 4d subshell.\(^3\)

The measurements of Hg photoemission cross sections\(^2\) indicated the existence of a large apparent discrepancy with theoretical calculations\(^4\) -\(^8\) for the 4f partial cross section, and lesser differences for the 5p and 5d cross sections. These findings were especially puzzling for the 4f subshell because of the concurrence of several theories,\(^6\) -\(^8\) and because it was expected that the calculations for the dominant 4f photoemission channel would not be complicated by large interchannel interactions.\(^8\) In addition, the same calculations predicted the angular distribution of Hg 4f photoelectrons quite well. For these reasons, we became suspicious that a significant systematic error was present in our cross-section measurements, with the unknown high-energy quantum yield of sodium salicylate being a plausible candidate.
We report here a measurement of a factor-of-two increase in the quantum yield of the visible scintillator sodium salicylate in the photon-energy range 80–270 eV, determined from a comparison of the relative quantum yield to the known energy dependence of the Ne 2p photoemission cross section. Similar measurements indicating the same qualitative behavior for the quantum yield of sodium salicylate have been obtained independently in two other laboratories. Using the newly measured quantum yield, we correct the previously reported cross sections for Hg and CH$_3$I.

Because the quantum-yield determination was made in the context of searching for a possible systematic error, Sec. II contains a description of the search which culminated in the measured variation in the relative quantum yield of sodium salicylate. Section III describes the corrections to the earlier photoemission data.

II. The Quantum Yield

The earlier photoelectron spectroscopy (PES) measurements were made with an angle-resolved time-of-flight (TOF) apparatus using synchrotron radiation from Beam Line III-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). To determine relative partial cross sections, one TOF analyzer placed at 54.7° with respect to the photon polarization vector measures photoemission peak intensities $I(h\nu)$ as a function of photon energy. The dependence of these intensities on experimental quantities in the dipole approximation is given by
where \( T(\varepsilon) \) is the relative transmission of the TOF analyzer as a function of electron kinetic energy \( \varepsilon \), \( p \) is the gas sample pressure, \( \sigma(h\nu) \) is the energy-dependent partial cross section, and \( N(h\nu) \) is the relative photon flux when the monochromator energy is set at \( h\nu \).

To determine unknown cross sections, knowledge of the analyzer transmission \( T(\varepsilon) \) is required. Qualitatively, the kinetic-energy dependence of \( T(\varepsilon) \) is governed by two effects. First, in the free-flight path from the interaction region to the channel-plate detector, the photoelectrons are influenced by residual stray magnetic fields and built-up electric charges, with the lowest-energy electrons being discriminated against. Second, after leaving the free-flight region, the electrons are accelerated by 100 volts before impacting a channel-plate detector. It is known\(^{14} \) that the channel-plate response is essentially constant throughout the electron-energy range applicable to this work. Considering these two contributions, \( T(\varepsilon) \) should increase monotonically with \( \varepsilon \), reaching an asymptotic value at high \( \varepsilon \). Previous observations have indicated that for all practical purposes \( T(\varepsilon) \) is constant for kinetic energies greater than 20 eV.

Quantitatively, 'calibration' of the 54.7° TOF detector [i.e. determining \( T(\varepsilon) \)] is accomplished by measuring photoelectron peak intensities as a function of kinetic energy for subshells with known partial cross sections, such as Ne 2p and 2s,\(^9 \) while simultaneously measuring the sample pressure and monitoring the photon flux with the
scintillator sodium salicylate. Figure 1 shows a $T(\epsilon)$ curve measured for Ne 2p photoelectrons (binding energy = 21.6 eV), plotted as a function of photon energy in the range 80-270 eV. The results in Fig. 1 were determined assuming a constant quantum yield for sodium salicylate. As noted above, at such high kinetic energies we expect the relative transmission of a TOF analyzer to be constant. To understand the apparent decrease of $T(\epsilon)$ by a factor of two, we start by rewriting Eq. (1):

$$T(\epsilon) \propto \frac{I(h\nu)}{p \sigma(h\nu) N(h\nu)}.$$  \hspace{1cm} (2)

Assuming that $T(\epsilon)$ should be constant for kinetic energies in Fig. 1 ($\epsilon > 58$ eV), we examine each factor on the right-hand side of Eq. (2). For the measured peak intensity $I(h\nu)$, we consider only those effects independent of the pressure, partial cross section, and photon flux, because those parameters are examined separately.

A major breakdown of the dipole approximation could lead to variations in $I(h\nu)$ measured at 54.7° with increasing photon energy, as the nondipole effects become increasingly more important. However, this possibility can be ruled out on several counts. Experimentally, no evidence for nondipole effects in the Ne 2p subshell has been observed in the 100-150 eV photon-energy range, and only small manifestations of such effects were seen at the much higher photon energies of 1254 and 1487 eV. Theoretically, only very small nondipole effects are expected for low-Z elements in the photon and photoelectron energy...
ranges pertinent to Fig. 1. Furthermore, the measured Ne cross sections and angular distributions are predicted well by theoretical calculations which assume the dipole approximation.

Another factor that could induce changes in $I(h\nu)$ would be a strongly energy-dependent photon polarization. However, the magnitude of the change in $T(e)$ shown in Fig. 1 would require a reversal of the synchrotron radiation linear polarization from horizontal to vertical in the 80-270 eV photon-energy range. Although the photon polarization has not been measured systematically for monochromators at SSRL, a large body of angular-distribution measurements made on Beam Line III-1 is inconsistent with anything but a high degree of horizontal linear polarization in this energy range. In addition the well-understood properties of synchrotron radiation argue strongly against a substantial variation in polarization.

Finally, we considered the possibility that some photon-beam movement as a function of photon energy caused the TOF analyzer to 'see' fewer electrons in its aperture-defined viewing region, while the photon-flux monitor, with a larger viewing area, saw no apparent change. We dismiss this explanation, however, because the simultaneous measurement of the relative efficiency $^{12}$ [i.e. ratio of transmissions $T(e)$] of two TOF analyzers at $0^\circ$ and $54.7^\circ$ (determined with the known Ne 2p angular distribution$^9$) was constant to within 2% over the same photon-energy range. The relative efficiency is as sensitive to changes in the experimental geometry as the transmission function $T(e)$ for the $54.7^\circ$ analyzer. This observation for the efficiency provides
an additional argument against the possibility of changing photon polarization.

The Ne pressure \( p \), monitored behind the nozzle which allows gas into the interaction region, was measured with a capacitance manometer to an estimated accuracy of \( \pm 2\% \). While it is a priori possible that the relationship between the measured pressure and the sample density in the interaction region is nonlinear, the flow of Ne was uninterrupted and steady for the results in Fig. 1. Furthermore, to guard against systematic changes, the points at different photon energies in Fig. 1 were obtained in a random order and repeated at random.

Moving on to the Ne 2p cross section \( \sigma(h\nu) \), the literature values are accurate to \( \pm 8\% \) or better over the entire energy range studied. In addition, the values are based on several independent determinations and compilations of the absolute total cross section of Ne.

A determination of the photon flux \( N(h\nu) \) for use in obtaining \( T(e) \) from Eq. (2) is predicated on the assumption that all of the photons in the synchrotron-radiation beam are of energy \( h\nu \). In general, higher-order (e.g. 2\( h\nu \)) and scattered (all energies) photons also are present, and will add to the apparent \( N(h\nu) \) with no concomitant increase in the measured peak intensity \( I(h\nu) \). Because higher-order contamination commonly provides the largest experimental uncertainty in intensity measurements using synchrotron radiation, small contributions from second-order radiation, detected by photoemission, have been corrected for carefully by the procedure described in the appendix. No photoemission induced by orders higher than second was observed in the
TOF spectra. A large contribution from scattered light is inconsistent both with the very low background in our photoelectron spectra and with measurements of the total photon flux in the vicinity of the carbon K edge. We estimate that scattered photons contribute at most 10%, and probably much less, to the total photon flux between 80 and 270 eV. No corrections for scattered-light intensity were made.

Determination of the relative synchrotron-radiation flux $N(h\nu)$ is accomplished by measuring the photocurrent from a photomultiplier tube (RCA 8850) which is sensitive to the visible fluorescence emitted by sodium salicylate after illumination by vacuum-ultraviolet photons. The quantum yield of sodium salicylate, $Q(h\nu)$, from 50 to 107 eV photon energy has been reported to be constant to within 5%, and we have assumed in earlier experiments that it remains so up to the carbon K edge. However, an increase in $Q(h\nu)$ at higher energies is expected because the quantum yield determined with X-rays is much larger than $Q(h\nu)$ below 107 eV. Such an increase in $Q(h\nu)$ could explain the behavior exhibited in Fig. 1, because the measured analyzer transmission $T(\epsilon)$ and the relative photon flux $N(h\nu)$ are inversely related [see Eq. (2)], and because our measurements of $N(h\nu)$ are directly proportional to $Q(h\nu)$. Other photon-flux variations are mitigated by the random data collection mentioned above. We note that variations in the photon flux due to the storage ring source and monochromator are properly accounted for in our normalization procedure.

Having exhausted other reasonable possibilities, we conclude that the changing quantum yield of sodium salicylate is the major cause of
the factor-of-two decrease in the measured $T(\epsilon)$ displayed in Fig. 1. Accordingly, we show in Fig. 2 the relative $Q(h\nu)$ derived from the measurements in Fig. 1. The increase exhibited in $Q(h\nu)$ in this energy range recently has been corroborated by Nordgren and Nyholm,\textsuperscript{10} and at least qualitatively by Samson,\textsuperscript{11} although our observation of an increase in $Q(h\nu)$ at energies as low as 80 eV may be in conflict with earlier measurements.\textsuperscript{1} We expect that different measurements of $Q(h\nu)$ may vary because of differences in experimental parameters, such as scintillator thickness, and differences in higher-order and scattered-light contributions to the incident radiation.

III. Implications for Photoemission Cross Sections

The consequences of this measurement of $Q(h\nu)$ for our cross-section results in this photon-energy range are obvious. Two previous studies yielded cross sections in this range for atomic Hg\textsuperscript{2} and CH\textsubscript{3}I.\textsuperscript{3} We have corrected these data for the $Q(h\nu)$ shown in Fig. 2, and the new results are shown in Figs. 3-6. We briefly discuss the implications of the new cross-section values.

The corrected Hg 4f cross-section data appear in Fig. 3. The delayed onset of the $4f \rightarrow \epsilon g$ channel is more pronounced now, and the agreement with theory is much improved. However, the calculated curves are still higher than the experimental data by approximately 50%. Due to uncertainties in photoabsorption measurements,\textsuperscript{21,22} the absolute scale of the Hg photoemission data could be off by as much as 30%,\textsuperscript{2} possibly explaining much of the discrepancy with theory. Regardless
of any correction in the normalization of the 4f data, the overall shape of the experimental curve will remain the same. We note that a rescaling of the data in Fig. 3 could not bring them into agreement with the Dirac-Slater curve, whereas the RRPA curve may be reconcilable with the 4f data in this way.

Another explanation which could account for the remaining difference between theory and experiment for the 4f cross section has been suggested for the relativistic random-phase approximation (RRPA) calculations. Because the RRPA equations include only single-ionization channels but require the calculated partial cross sections to sum to the correct integrated oscillator strength, it might be expected that the calculations will overestimate inner-shell cross sections for cases in which significant multi-electron processes (i.e. double excitation and ionization) are occurring. No experimental data for Hg double excitation or ionization are available in this energy range to check this hypothesis.

Figures 4 and 5 show mixed changes in agreement with theory for 5p and 5d photoemission from Hg, respectively. The agreement for the 5p channels is very good, and the Cooper minima in these channels are now more apparent. However, the corrected 5d cross section deviates substantially from the theoretical curves at the highest energies; the 5d Cooper minimum shows up experimentally as a true cross-section minimum. Considering the set of Hg partial cross sections in Figs. 3-5, it is clear that no single renormalization of the data can reconcile the available theoretical calculations with our corrected results.
The I 4d cross section of CH$_3$I, shown in Fig. 6, exhibits an enhancement in the observed Cooper minimum after application of the correction for the sodium salicylate quantum yield. There are no theoretical calculations for this subshell available for comparison.

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Appendix: Correction of the Relative Transmission for Second-Order-Light Contributions to the Photon Flux

The values of $T_0(\epsilon) \left[ T_0(h\nu)^{24} \right]$ (subscript zero denotes uncorrected values) determined from Eq. (2) without correcting for second-order-light contributions to $N_0(h\nu)$ (not shown) exhibit a similar qualitative trend with photon energy as shown by the corrected values of $T(h\nu)$ in Fig. 1, because the fraction of photons that are
second order is relatively small (≤15%) for most of this energy range. Quantitatively, the decrease with energy of $T_0(h\nu)$ is suppressed, necessitating the second-order correction described below.

The determination of the relative amount of second-order light is accomplished by comparison of the peak intensities, $I(h\nu)$ and $I(2h\nu)$, for Ne 2p photoemission induced by first- and second-order radiation in each TOF spectrum. The ratio of peak intensities [see Eq. (1)] measured when the monochromator is set at $h\nu$ is given by:

$$\frac{I(2h\nu)}{I(h\nu)} = R(h\nu) \cdot \frac{\sigma(2h\nu)}{\sigma(h\nu)},$$

(A1)

where $R(h\nu)$ is the ratio of second- to first-order flux, $N(2h\nu)/N(h\nu)$. The values of $R(h\nu)$ derived from Eq. (A1) can be used to correct the measurement of the relative photon flux $N_0(h\nu)$, if care is taken to recognize that the first- and second-order contributions to $N_0(h\nu)$ are weighted differently, with relative weights equal to $Q(h\nu)$ and $Q(2h\nu)$, respectively.

We start by assuming that the change of the relative transmission above 80 eV photon energy is the result of a change in $Q(h\nu)$ only. The correction to $T_0(h\nu)$ due to second-order-light contributions to $N_0(h\nu)$ can be written [see Eq. (2)]:

$$T(h\nu) = \frac{T_0(h\nu) N_0(h\nu)}{N(h\nu)} = T_0(h\nu) \left[ 1 + R(h\nu) X(h\nu) \right] \alpha \frac{1}{Q(h\nu)},$$

(A2)

$$X(h\nu) = \frac{Q(2h\nu)}{Q(h\nu)} = \frac{T(h\nu)}{T(2h\nu)},$$

(A3)
where \( X(h\nu) \) represents the relative weighting of the contributions to
\( N_0(h\nu) \) of photons of energy \( 2h\nu \) and \( h\nu \). The following steps yield
the corrected values \( T(h\nu) \):

1. For \( h\nu = 150, 160 \text{ eV} \), no second-order Ne 2p photoemission was
discernible [i.e. \( R(h\nu) \ll 1\% \)], because the second-order energies of 300
and 320 eV were absorbed by a carbon window.19

2. Combining Eqs. (A2) and (A3), solving for \( T(h\nu) \), and using
\( T(160) \) from step 1 we find, for \( h\nu = 80 \text{ eV} \):

\[
T(80) = T_0(80) \left[ 1 - C(80) \right]^{-1},
\]

\[
C(80) = \frac{T_0(80) R(80)}{T(160)}.
\]  

3. For photon energies above 160 eV, we assume \( 1.5 \leq X(h\nu) \leq 2.5 \),
yielding \( T(h\nu) \) for 170-270 eV using Eq. (A2). This large range of
values for \( X(h\nu) \) is consistent with measurements10 of \( Q(h\nu) \) above
300 eV, and with the present results at lower energies, and introduces
only small errors in the corrected \( T(h\nu) \) because the amount of
second-order light for \( h\nu \geq 170 \text{ eV} \) is small (2-10\%).

4. Having determined the corrected values for \( h\nu \geq 170 \text{ eV} \) in step
3, we use them in Eq. (A4) for \( h\nu = 90, 100, 110, \text{ and } 130 \text{ eV} \).

The final results, corrected for second-order contributions as
outlined above, are shown in Fig. 1.
References


19. The experimental apparatus was separated from the monochromator by a thin carbon window, which absorbs very strongly at the carbon K edge starting at $-280$ eV. Because most of the total photon flux was absorbed by the window at this edge, it is clear that most of the photons were first-order, rather than higher-order or scattered photons.


24. We use the symbol $T(h\nu)$ in place of $T(\epsilon)$ for the relative transmission because we are trying to determine $Q(h\nu)$, which produces a photon-energy-dependent effect on the relative transmission. For calibration with Ne 2p photoelectrons, $T(h\nu) = T(\epsilon + 21.6 \text{ eV})$.

Figure Captions

Figure 1. Relative transmission function $T(\varepsilon)$ for the $54.7^\circ$ TOF analyzer determined with Ne 2p photoelectrons shown as a function of photon energy, after correction for second-order contributions to the synchrotron-radiation flux as described in the appendix. The Ne 2p binding energy is 21.6 eV, so that the lowest kinetic energy represented is approximately 58 eV. The average of the two lowest-energy points has been normalized to unity.

Figure 2. Relative quantum yield of sodium salicylate $Q(h\nu)$ versus photon energy, taken as the inverse of the results in Fig. 1. The line is a linear least-squares fit to the data, described by $Q(h\nu) = 0.576 + 0.0056(2)h\nu$, for $80 < h\nu < 270$ and with $h\nu$ expressed in eV.

Figure 3. Hg 4f cross section (Ref. 2) after correction for the changing quantum yield of sodium salicylate. The solid and dashed curves are RRPA (Ref. 7) and Dirac-Slater (DS-Ref. 8) calculations, respectively.

Figure 4. Hg $5p_{3/2}$ and $5p_{1/2}$ cross sections as in Fig. 3.

Figure 5. Hg 5d cross section as in Fig. 3. Dashed-dotted curve is from absorption measurements (Refs. 21 and 22). The low-energy solid curve is also a RRPA calculation (Ref. 25).

Figure 6. CH$_3$I 4d cross section (Ref. 3) after correction for the changing quantum yield of sodium salicylate.
Figure 1

Relative transmission vs. Photon energy (eV)

T(\epsilon)

XBL 8510-4393
Figure 2

Sodium salicylate

Relative quantum yield

\[ Q(h\nu) \]

Photon energy (eV)

50  100  150  200  250
Figure 3

Hg 4f

Cross section (Mb)

Photon energy (eV)
Figure 4
Figure 5

Cross Section (mb)

Hg 5d

Photon energy (eV)

0 0.1 1 10

Expt DS RRPA
Figure 6

CH$_3$I: I (4d)
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