Theoretical Fitting of the Argon K Absorption Spectrum on a One-Electron Model*

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The one-electron model was used to analyze the argon K absorption spectrum near the K edge. It was assumed that the absorption spectrum consists of (1) two Lorentzians due to $1s \rightarrow 4p$ and $1s \rightarrow 5p$ resonant transitions, (2) a modified arctangent to account for the $1s \rightarrow np$ ($n \geq 6$) and the $1s \rightarrow$ continuum transitions, and (3) a constant background due to the L, M ionizations. The transmission spectrum containing adjustable parameters was constructed on the one-electron model and was then smeared by the experimental window function. The values of these parameters were selected to minimize the χ^2 value between the observed transmission curve and the smeared-model transmission curve. The criterion showed that the present model fits the observed curve. Pertinent parameters were interpreted in terms of oscillator strengths and the K-state width. The oscillator strengths (0.00217 and 0.00066) of the $1s \rightarrow 4p$ and $1s \rightarrow 5p$ transitions show fair agreement with the theoretical values (0.00166 and 0.00053). The K-state width parameter is 0.68 eV, which compares well with the value obtained by several different spectral methods as well as the value obtained from the K fluorescence yield.

I. INTRODUCTION

THE conventional interpretation of x-ray spectra concerns mainly the energies and relative intensities of observed spectra. Both for emission and absorption spectra the basic idea in the analysis lies in the one-electron model from which an x-ray energy diagram may be constructed to explain most of the dominant absorption and emission lines. However, the experimental values of the absolute intensities of the absorption and emission lines have not been satisfactorily correlated with theory. This is because the experimental data are not accurate enough to give dependable values of absolute intensity and because sufficiently accurate wave functions have not so far been calculated.

One of our purposes in this study is to use the one-electron model to analyze the K x-ray absorption spectrum and to check the validity of the model by means of the χ^2 test. As a result of the analysis we are able to determine experimentally the characteristics of oscillator strengths, and x-ray state widths. These physical quantities are then compared with some theoretical values or values obtained by independent methods.

The K absorption spectrum for gaseous argon near its K edge has been measured by several investigators.[1–5] The measurements by Parratt[1] and Schnopper[2] were carried out with a two-crystal x-ray spectrometer, and the present analysis is applied to the latter's results. Schnopper's absorption spectrum is shown in Fig. 1. There is clear evidence of resonance absorption lines in the spectrum and these, by Parratt's analysis, are on the low-energy side of the K edge, i.e., of the $1s \rightarrow$ continuum edge.

In analysis of the observed spectrum it is necessary to take account of the fact that the finite resolution of a spectrometer always gives rise to a smearing of the true spectrum. If $O(E_n)$ represents the function actually observed at points E_n, and $T(E)$ represents the true function, then the smearing may be expressed by the convolution integral

$$O(E_n)=\int_{-\infty}^{\infty} T(E)W(E_n-E)dE, \qquad (1)$$

where $W(E_n-E)$ is the smearing function.

For the measurements with a two-crystal spectrometer with both crystals reflecting in first order, $W(E_n-E)$ may be approximated by the $(1,-1)$ rocking curve, and, therefore, in principle, $T(E)$ can be determined by unfolding $W(E_n-E)$ from the observed $O(E_n)$ by means of an iteration. In practice, however, both $O(E_n)$ and $W(E_n-E)$ are not well-known analytic functions but contain experimental errors, and because of this no unique solution can be found for $T(E)$. In particular, in the present case, a conventional iteration procedure[2,6] converges very slowly since the width of $W(E_n-E)$ is of the same order of magnitude as that of the true spectrum. This fact also causes another quite significant disadvantage in the unfolding procedure, i.e., the accumulation of errors at each point. It is inevitable that the fluctuations will multiply in each iteration.

In the present study the difficulties cited above are avoided by folding the $(1,-1)$ window into a transmission curve T_{model} which is an analytic function

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[5] J. A. Soules and C. H. Shaw, Phys. Rev. **113**, 470 (1958).

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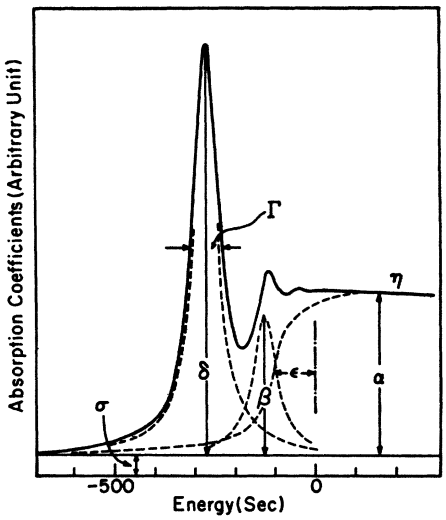

FIG. 1. K x-ray absorption spectrum of argon (taken by H. Schnopper) corrected for the window. The Greek letters indicate the parameters used in the data analysis.

constructed on the basis of the one-electron model. Hence, the smeared curve $O_{\text{model}}(E)$ which is to be compared with the experimentally observed $O(E)$ includes the instrumental smearing effect, and we do not increase the error in an unfolding procedure.

To construct T_{model} we assume that the final state of the x-ray-excited K electron is either one of the unoccupied bound orbitals or the continuum (photoelectric) state. We introduce in T_{model} seven adjustable parameters which have simple physical meanings. These are then fixed so as to minimize the χ^2 value between O_{model} and $O(E)$. Finally, the seven *experimentally* determined parameters are interpreted in terms of oscillator strengths and the K-state widths, and compared with theoretical values.

II. ANALYSIS OF EXPERIMENT

The ground-state electronic configuration of argon is

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$$

and upon the production of a K hole the excited electron moves to one of the np ($n\geq 4$) bound orbitals, or to the continuum of unbound hyperbolic orbitals. According to Parratt the first two peaks observed on the low-energy side (see Fig. 1) are attributed to the $1s\rightarrow 4p$ and $1s\rightarrow 5p$ resonant transitions of the excited electrons. The energy separation of these two x-ray-excited states is found to agree with that of the Hartree-Fock energies[7] of the $4p(-2.72$ eV) and $5p(-1.27$ eV) excited states of a potassium atom. Based on this fact the K ionization edge (the energy zero) is set at 2.72 eV above the first absorption peak.

In the present x-ray absorption spectrum the line width of a resonance absorption is mainly determined by the lifetime broadening of the K hole. If we assume an *exponential decay* of the excited states, we may approximate the *shape* of a resonance line by a Lorentzian function $L(x,x',\Gamma)$, which is defined by

$$L(x,x',\Gamma)=\frac{\text{constant}}{1+4[(x-x')/\Gamma]^2}. \tag{2}$$

Here, $L(x,x',\Gamma)$ is centered at $x=x'$, and Γ is the full width at half-maximum.

The contribution of all resonant transitions to the absorption coefficients $\mu_R(E)$ is given by

$$\mu_R(E)=\sum_{n=4}^{\infty} A_n L(E,E_n,\Gamma). \tag{3}$$

For convenience we rewrite this as

$$\mu_R(E)=\frac{\delta}{1+4[(E-E_4)/\Gamma]^2}+\frac{\beta}{1+4[(E-E_5)/\Gamma]^2}+\sum_{n=6}^{\infty} A_n L(E,E_n,\Gamma), \tag{4}$$

where δ, β and Γ correspond to those in Fig. 1.

For the electronic transition to the continuum state (i.e., the photoelectric transition) the absorption coefficient μ_C near the K ionization edge may be expressed by

$$\mu_C(E)=\int_0^{\infty}\frac{B(E')}{1+4[(E-E')/\Gamma]^2}dE'. \tag{5}$$

$B(E')$ is now a continuous function of E' and, except for a proportionality constant, is the oscillator density in the photoelectric effect.

It is assumed here that the contribution of the infinitely many bound states to the absorption coefficients near the K ionization edge—the last term of (4)—is indistinguishable from that of the continuum state $\mu_C(E)$. That is, for large n, the function $A_n/(E_n-E_{n-1})$ matches $B(E')$ smoothly near the edge. In fact, this relation has been proved theoretically for the hydrogen case,[8] and, since the asymptotic nature of the effective potential for the excited electron is essentially hydrogen-like, this assumption should be reasonable. Then, the sum of $1s\rightarrow np$ ($n\geq 6$) resonant transitions is approximated by extending the integral of (5) into the lower side of the edge by an amount ϵ. This approximation should be good considering that even for the $5p$ and $6p$ states the energy separation is smaller than the line width Γ. Actually we have ϵ as a parameter, to be determined empirically. As we expect ϵ turns out to be between the $5p$ and $6p$ levels. This could be considered a consistency check.

[7] L. Bierman and K. Lübeck, Z. Astrophys. **25**, 325 (1949).

[8] Y. Sugiura, J. Phys. Radium **8**, 113 (1927).

The total absorption coefficient μ_{total} is then

$$\mu_{\text{total}}(E)=\mu_R+\mu_C+\mu_{L,M}$$
$$=\frac{\delta}{1+4[(E-E_4)/\Gamma]^2}+\frac{\beta}{1+4[(E-E_5)/\Gamma]^2}$$
$$+\int_{-\epsilon}^{\infty}\frac{B(E')}{1+4[(E-E')/\Gamma]^2}dE'+\sigma, \quad (6)$$

where $\mu_{L,M}$ is the absorption coefficient due to the L, M ionization. Considering the slope observed on the high-energy side of the K ionization edge we choose empirically for $B(E')$ near the edge

$$B(E')=\alpha/(1+E'/\eta). \quad (7)$$

Because of the denominator the integral involved in (6) is only sensitive to $B(E')$ near the edge. Substitution of (7) into (6) gives

$$\mu_{\text{total}}(E)=\frac{\delta}{1+4[(E-E_4)/\Gamma]^2}+\frac{\beta}{1+4[(E-E_5)/\Gamma]^2}$$
$$+\alpha F(E-\epsilon,\Gamma,\eta)+\sigma, \quad (8)$$

where

$$F(x,\Gamma,\eta)=(1+2(x/\Gamma)+(x/\Gamma)^2)^{-1}$$
$$\times\left[\frac{1}{\pi}\frac{\Gamma}{4\eta}\ln\left\{\left(\frac{\Gamma}{2\eta}\right)^2+\left(\frac{x}{\eta}\right)^2\right\}\right.$$
$$\left.+\left(1+\frac{x}{\eta}\right)\left\{\frac{1}{2}+\frac{1}{\pi}\tan^{-1}\left(\frac{2x}{\Gamma}\right)\right\}\right]. \quad (9)$$

The transmission curve constructed on the basis of the present model, $T_{\text{model}}(E)$, is given by

$$T_{\text{model}}(E)=\exp[-P\mu_{\text{total}}(E)], \quad (10)$$

where P is an absorber pressure, and for convenience $P=35$ mm Hg is taken to be a unit. δ, β, α, σ, and P involved in (10) are taken to be dimensionless quantities. Equation (10) is then substituted for $T(E)$ in Eq. (1) to obtain $O_{\text{model}}(E)$.

The instrumental window function $W(E)$ is approximated by the $(1,-1)$ rocking curve of calcite crystals, which is truncated at ten half-widths from the center. The significant effect of the use of a truncated window function appears in the region where the transmission curve $T_{\text{model}}(E)$ has a strong contrast. At low pressure the contrast of $T_{\text{model}}(E)$ varies linearly proportional with pressure, and is reduced to zero at zero pressure. Therefore, this effect would become the minimum in the limit $P\rightarrow 0$.[9]

In the present treatment the smeared transmission curves $O_{\text{model}}(E)$ are numerically constructed from Eq. (1) by means of Simpson's rule for three different pressures. The three sets of $O_{\text{model}}(E)$ are analyzed separately to determine the set of parameters that gives the best all around fit to the observed curve $O(E)$. Thus, a different set of parameters is obtained for three different pressures. Each parameter is then plotted against pressure and extrapolated to zero pressure. The intercept at zero pressure is interpreted as a fully corrected value of this parameter.

The goodness of fit between the *observed* transmission curve $O(E)$ and the smeared-model transmission curve $O_{\text{model}}(E)$ is checked carefully by calculating the χ^2 for a given set of the seven parameters in Eq. (8). The observed transmission curve $O(E)$ consists of 180 data points. Then, the number of degrees of freedom is 172 since the model uses seven parameters to approximate the observed curve, and the relative standard error obtained from the experiment is assumed to be a constant. We take the confidence limit at 95%. The best values of the parameters are taken to be those which give the minimum value in χ^2, and are

$$\begin{aligned}&\alpha=0.255\pm0.005\\&\delta=0.70\pm0.01\\&\beta=0.215\pm0.15\\&\Gamma=72.0\pm1.5\text{ sec of arc}\\&\epsilon=100.0\pm6.0\text{ sec of arc}\\&\sigma=0.030\pm0.001\\&\eta=5500.0\pm1500.0\text{ sec of arc.}\end{aligned} \quad (11)$$

Here, 105 sec of arc corresponds to 1 eV. These are the *experimental values* of the seven parameters which are introduced on the basis of the one-electron model.

In terms of μ_{total}—(8)—with the set of parameters given by (11) the physical mass absorption coefficients μ_m (in cm^2/g) may be analytically approximated by

$$\mu_m(E)=\frac{760}{35}\frac{1}{l\rho_0}\mu_{\text{total}}(E), \quad (12)$$

where l is the absorber length ($=2.54$ cm) and ρ_0 the density of argon at room temperature. We have the atomic cross section σ_{total}:

$$\sigma_{\text{total}}(E)=(A/N_0)\mu_m(E). \quad (13)$$

Here, N_0 and A represent Avogadro's number and the atomic weight of argon, respectively.

III. INTERPRETATION OF PARAMETERS AND COMPARISON WITH THEORETICAL RESULTS

Oscillator Strengths

The oscillator strength for the resonant transition may be obtained experimentally by evaluating the area under the observed atomic cross section. Denoting by

[9] L. G. Parratt, C. F. Hampstead, and E. L. Jossem, Phys. Rev. **105**, 1228 (1957).

σ_R the atomic cross section (in cm^2) we have

$$f_{n,n'}=\left(\frac{2\pi^2e^2\hbar}{mc}\right)^{-1}\int_{\text{line}}\sigma_R(E)dE, \qquad (14)$$

where $f_{n,n'}$ is the oscillator strength for the $n\rightarrow n'$ resonant transition.

In the present analysis the $1s\rightarrow 4p$ and $1s\rightarrow 5p$ resonant transitions are characterized by δ, β, and Γ. By integrating the Lorentzians for these transitions we obtain

$$f_{1s,4p}=6.18\times10^{-2}\delta(\Gamma/\text{Ry})$$

and

$$f_{1s,5p}=6.18\times10^{-2}\beta(\Gamma/\text{Ry}).$$

The use of the corrected values of δ, β, and Γ gives the experimental values of these oscillator strengths as listed in Table I.

TABLE I. Oscillator strengths $f_{1,4}$ and $f_{1,5}$.

	$f_{1,4}$	$f_{1,5}$
Theoretical value	1.66×10^{-3}	0.53×10^{-3}
Experimental value[a]	$(2.17\pm0.13)\times10^{-3}$	$(0.66\pm0.07)\times10^{-3}$

[a] The previous values [T. Watanabe, Bull. Am. Phys. Soc. 7, 339 (1962); Res. Rept. No. 12, AFOSR 2254 (unpublished)] $(1.8\pm0.2)\times10^{-3}$ for $f_{1,4}$ and $(0.57\pm0.10)\times10^{-3}$ for $f_{1,5}$ were obtained by use of the experimental data corrected for the window by Schnopper (Ref. 2) without consideration of the pressure effect.

On the one-electron model the corresponding theoretical values of the oscillator strengths are given by

$$f_{1s,np}=\tfrac{2}{3}|E_{1s}-E_{np}|\,|\langle 1s|r|np\rangle|^2K^2, \qquad (15)$$

where

$$\langle 1s|r|np\rangle=\frac{1}{a_0}\int_0^\infty r^3R_{1s}(r)R_{np}(r)dr. \qquad (16)$$

$R_{1s}(r)$ and $R_{np}(r)$ are the radial wave functions of the $1s$ and np orbitals, respectively. The energies E_{1s} and E_{np} are in rydbergs. K is a correction factor which takes account of the effect of the core electrons.

In evaluating the dipole moment (16) we take for the $1s$ wavefunction the Hartree-Fock function of normal argon.[10] For the excited states we take the $4p$ and $5p$ electron wave functions of an excited potassium atom obtained by Beirmann and Lübeck.[7] Numerical calculations give

$$\langle 1s|r|4p\rangle=3.23\times10^{-3}$$

and

$$\langle 1s|r|5p\rangle=1.83\times10^{-3}.$$

The energies of the $1s$, $4p$, and $5p$ states are taken to be 237.2, 0.2004, and 0.093 Ry, respectively. The theoretical oscillator strengths arrived at in this way are listed under "theoretical values" in Table I. Here, K is taken to be unity.[11]

The theoretical values of the x-ray oscillator strengths for both transitions are about 25% less than the experimental values in the present approximation. However, the ratio $f_{1s,4p}/f_{1s,5p}$ is in good agreement and is also consistent with the theoretical value calculated by Vainstein *et al.*[12] by means of the "quantum defect" method.

K-State Width

From the parameter Γ the experimental line width is determined to be 0.68 ± 0.03 eV. Since the initial state is the ground state of an argon atom, the observed linewidth can be attributed almost entirely to the lifetime broadening of the K state. This value is almost 30% larger than the value quoted by Parratt,[1] which was obtained by essentially the same method.

The K-state width has been estimated by other spectroscopic methods. Deslattes[13] measured the K-β emission spectrum of argon with a two-crystal x-ray spectrometer and estimated the K-β linewidth as 0.70 ± 0.05 eV after correction for instrumental resolving power. In this case, if this line is a simple singlet, the linewidth is almost entirely the width of the K state because the M state width can be neglected in comparison.

Several investigators obtained empirical formulas for the state width using series of independent experimental data on the emission linewidths and on the fluorescence yield. Blokhin and Sachenko[14] estimated the K width of argon to be 0.63 eV, and Meisel and Nefedow[15] obtained 0.70 eV. Callan,[16] assuming the Z^4 dependence of the radiative width, estimated the width to be 0.64 eV. These values, although they were not determined by a direct measurement, are in good agreement with the present value.

The theoretical evaluation of the K-state width is rather complicated because it becomes necessary to calculate the transition probabilities of all possible transitions involving the K hole. However, the use of the K-fluorescence yield (experimental) and the theoretical value of the K radiative width provide some estimate of the K width. If the radiative width, Γ_K, calculated by Bagus[11] (=0.0835 eV) and the latest

[10] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **166**, 450 (1938).

[11] It has been shown that the introduction of electron-hole interactions can increase a value for the $1s\rightarrow 3p$ dipole matrix element by 30% compared to that calculated in the Hartree-Fock approximation. If this were the case for the $1s\rightarrow np$ ($n\geq4$) matrix elements the oscillator strength calculated including effects of the $1s$ hole would be in better agreement with the experimental value: See P. S. Bagus, Argonne National Laboratory report ANL-6959, 1964 (unpublished).

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[13] R. Deslattes, Phys. Rev. **133**, A390, 399 (1964).

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[16] E. J. Callan, Phys. Rev. **124**, 993 (1961); Bull. Am. Phys. Soc. **7**, 416 (1962).

value of the K-fluorescence yield ω_K ($=0.14\pm0.014$), by Watanabe, Schnopper and Cirillo[17] are used, the K width ($\Gamma=\Gamma_K/\omega_K$) is estimated to be 0.60 ± 0.06.[18]

IV. DISCUSSION AND CONCLUSION

The use of the $4p$ and $5p$ Hartree-Fock energies of an excited potassium atom appears to be a good approximation to the present case. This may imply that the x-ray-excited K electron of argon experiences a potential similar to that of the outer electron of a potassium atom outside a filled core.

The parameters α, σ, and η give the characteristics of the absorption spectrum very near the photoelectric threshold (K ionization edge). However, since there is no calculation of the Hartree-Fock wave function for the continuum state near the edge (i.e., for small positive energy), we are unable to make comparison with theory. It is deemed desirable to obtain the wave function of the excited K electron for both bound and continuum state as well as to justify the assumption made on the continuity of the oscillator density at the ionization edge.

It is shown that two Lorentzians combined with a modified arctangent and a constant background can explain the K x-ray absorption spectrum of argon. It has been shown[19] that, if the decay rate of an excited state is fast, the intensity distribution may not follow a Lorentzian. One interpretation of the present analysis would be that the K x-ray-excited state of argon still follows an exponential decay.

The K-state width is determined as 0.68 eV from the present analysis. This is probably the most reliable value among those estimated from analysis of experimental x-ray spectra.

The oscillator strengths for the $1s \rightarrow 4p$ and $1s \rightarrow 5p$ transitions are found to be 2.17×10^{-3} and 0.66×10^{-3}, respectively. They are about 25% larger than the values calculated in the present approximation.

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[17] T. Watanabe, H. W. Schnopper, and F. N. Cirillo, Phys. Rev. **127**, 2055 (1962).

[18] The error quoted is entirely due to the error in $\bar{\omega}_K$.

[19] R. C. Winter, Phys. Rev. **123**, 1503 (1961).

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Nuclear Magnetic Resonance in Liquid He^3

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The nuclear magnetic susceptibility χ of liquid He^3 has been studied as a function of temperature (0.07 to 4.2°K) and pressure (0.7 to 27.5 atm). It has been found that Curie's law holds above 2°K, where the experimental results showed an rms deviation of less than 1.5%. At 1.1°K the liquid is (5 ± 1.5)% degenerate; no pressure dependence of χ could be detected above 1.2°K. As the temperature is reduced below 1.1°K, the product χT falls monotonically and χ tends towards the constant zero-temperature limiting value; χ increases with increasing pressure in this temperature range and values of T_F^{**}, the magnetic degeneracy temperature, as a function of pressure are given. The low-temperature results are considered in the light of the Fermi-liquid theory of Landau and its extension to finite temperatures. A plot of reduced susceptibility versus reduced temperature, of the type suggested by Goldstein, indicates that data at all pressures and temperatures may be described closely (within 3%) by a single function. Comparison of this work is made with published results from other laboratories. The spin-lattice relaxation time has also been investigated over the same pressure and temperature ranges, and lower limits for $(T_1)_{\text{bulk}}$ at low temperatures have been deduced. An analysis of the type suggested by Low and Rorschach was applied for this purpose. The results are the first reported in the Fermi-liquid region, and at higher temperatures they are compared with data published elsewhere. Low-temperature thermometry was facilitated by measurement of the nuclear susceptibility of F^{19} in a calcium fluoride crystal immersed in the liquid He^3.

I. INTRODUCTION

SINCE the early measurements of Fairbank[1] the nuclear susceptibility χ of liquid He^3 has been studied in several laboratories.[2–4] Measurements below 0.1°K have shown that χ tends towards a constant

[1] W. M. Fairbank and G. K. Walters in *Proceedings of the Symposium on Liquid and Solid He^3* (Ohio State University Press, Columbus, Ohio, 1958), Suppl., p. 1.

[2] A. L. Thomson, H. Meyer, and E. D. Adams, Phys. Rev. **128**, 509 (1962).

[3] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. **127**, 671 (1962).

[4] H. A. Schwettman and H. E. Rorschach, Jr. (to be published).