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Relative Energy Measurements in the K Series of Argon

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The relative positions of the principal features of the emission and absorption spectra of argon in its K series have been measured. The energy difference between the K-series Rydberg limit and the peak of $K\beta_{1,3}$ is compared with the optical ionization potential. Location of the K-series limit via the experimental ionization potential leads to new values for the L_{II} and L_{III} terms from measurements of $K\alpha_2$ and $K\alpha_1$. These are in reasonable agreement with Hartree-Fock calculations, and with recent grating measurements from other laboratories and single-crystal measurements newly reported here.

I. INTRODUCTION

The wavelengths of the more prominent features of the argon spectrum in K-series emission were determined long ago using a discharge source.[1] The violence of this type of excitation gives rise to a certain concern as to whether the results would carry over to a tenuous source, minimally disturbed. Moreover, these early photographic measurements did not go far toward establishing line profiles. More recent measurements[2] carried out in fluorescence have delineated some of the emission profiles with greater precision and revealed at least one line not previously reported.

The K-series absorption spectrum has been the subject of several studies of considerable precision with regard to profiles and relative energy positions of the absorption features.[3] The most recent measurements[4] have been carried out with sufficient delicacy to show, in addition to the main threshold absorption structure, features occurring near the thresholds for double vacancy production.

Unfortunately, these measurements have been carried out in such a way that a precise correlation of the wavelength scales for emission and absorption spectra is not possible. It is the aim of the present paper to connect the existing profile measurements in emission and absorption by a consistent relative energy scale. No attempt is made to amplify or improve on the detailed profiles already reported or to improve the absolute wavelength values. The present measurements were undertaken solely in an attempt to carefully relate in energy the more prominent features of the emission and absorption spectra.

II. EXPERIMENTAL DETAILS

The measurements reported here were carried out on a vacuum two-crystal instrument[5] using calcite crystals. Emission spectra were excited in fluorescence by a primary x-ray source[6] using a gold-plated anode at 3 kW. The source density and that in the proportional-counter detector were stabilized by pycnostats[7] with flow rates of the order of 1 atm cm^3/sec. Absorption features were located by means of the counter-efficiency procedure[8] with the same experimental arrangement except that, in this case, the primary anode was viewed directly by the spectrometer.

The spectrometer provided for coordinated rotation of crystals, source, and detector by means of stepping motors. The angular range available was limited to 8° in Bragg angle by the tangent drives which rotate the two crystals. Since, at the time of these measurements, the instrument was not equipped with a precision circle, only energy differences within the tangent drive range could be measured. Data were recorded in a step-scan procedure and stored on paper tape.

III. DETERMINATION OF A LOCAL ENERGY SCALE

On account of the nonlinear character of the Bragg relation, determinations of energy (or wavelength) differences inevitably require knowledge of the absolute angles involved. However, if the differences are not large, estimates of absolute angle need not be very precise. The dihedral angle associated with a particular pair of (equal) settings for the tangent drives may thus be obtained from any accessible reference line if a sufficiently good *d* value is available for the crystals in use. In particular, as will be seen below, the available data on the lattice parameter of calcite (assuming "worst case" errors), together with previous measurements of the wavelength of Ar$K\alpha_1$ (again assuming worst case errors), are sufficient to provide energy differences within the *K* series that have errors no larger than 0.05 eV.

Starting from an engagement of the drives at a nominal 40° Bragg angle, a local energy scale was established by a rather straightforward refinement. The derived energy scale has significant error contributions from the following sources: (1) instrument assembly, $3\sigma = \pm 0.0004$ Å*; (2) assumed wavelength (4.1418 Å*) of Ar$K\alpha$[9]; with 3σ estimated at ±0.0002Å*; (3) grating space for calcite (3.035 Å*) (range of reported values[10] suggests 3σ may be ±0.0002 Å*). Items (2) and (3) imply that the Bragg angle for Ar$K\alpha_1$ is $(43.6632 \pm 0.005)°$ (3σ) from which one can deduce that the engagement angle (nominally 40°) was $(40.0227 \pm 0.005)°$ (3σ).

The remaining spectral features have been located relative to the above-determined engagement angle through the arctan correction required of the drive system, using the *d* value given above. The output of this procedure is a set of wavelength values, with which is associated a set of energy values through the current conversion, 12398.10 ±0.14 Å* eV (P. E.).[11] The resulting energy table carries a large uncertainty in each entry owing to the various errors noted above, in addition to the uncertainty in the conversion factor. The differences in energy, however, carry a smaller absolute uncertainty, since the errors are highly correlated and the energy differences are small compared to their absolute magnitudes. Similar considerations indicate that the index of refraction and temperature corrections may be neglected in their effect on the energy differences.

IV. RESULTS AND DISCUSSION

The more prominent spectral features of the *K* series are indicated on a broken energy scale in Fig. 1. The left-hand group of features are the $K\alpha_2, K\alpha_1$, and $K\beta_{1,3}$ emission lines. To the right is an indication of the absorption spectrum which shows peaks corresponding to a Rydberg series $1s \to 4p, 1s \to 5p, \ldots, 1s \to \infty p$. Energy intervals indicated by the upper numerical values are those determined by experiment. The lower numbers will be discussed below.

Energy-term values are of primary interest in what follows. These are to be understood in the classical sense of x-ray work as energies corresponding to the (relaxed) state of an atom with a vacancy in one of its shells and an electron at rest at infinity. Allowed single-vacancy x-ray transitions (for example, the lines shown in Fig. 1) connect these levels. Thus, if one of the levels is known and the emission spectrum is measured, the remaining levels are thereby determined. It is evident that at least one level on the x-ray energy-level diagram (i.e., the lowest one) will also occur on the optical energy-level diagram as the first ionization potential. The optical level diagram connects with the ground state, hence, the entire single-vacancy diagram can be constructed by this connection.

Thus, in Fig. 1, the energy of the *K* state, i.e., the bottom of the *K*-shell photoionization continuum is located at an optical ionization potential of[12] 15.75 eV[12] above $K\beta_{1,3}$. An alternative procedure for locating the *K*-state energy is to estimate the $4p \to \infty p$ interval and add this to the energy of the $1s \to 4p$ resonance. This is indicated in Fig. 1 with the 2.70-eV value for $4p \to \infty p$ previously used.[13] The resulting estimate of the *K*-state energy exceeds that given above (by what appears to be a more reliable procedure) by 0.17 eV.

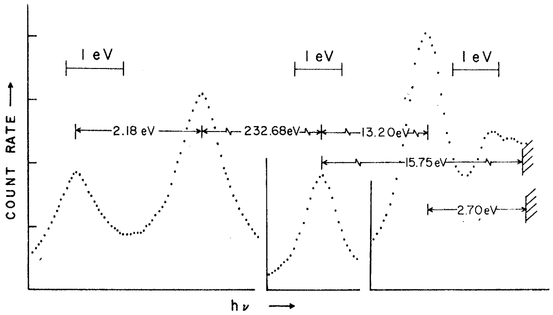

FIG. 1. Principal features of the *K* spectrum of argon on a segmented scale. Note that data were taken at equal steps of 0.01° in Bragg angle.

The problem here has mostly to do with the estimate for the energy interval $4p \to \infty p$. The 2.70-eV number has been around for many years. It can be obtained from the familiar assumption that the terms in the presence of a K vacancy should be as they are in the atom $Z+1$, i.e., the np terms of the potassium I system.[13, 14] The same numerical value can be obtained by a quantum-defect procedure, assuming that the quantum defect is the same for all states in the Rydberg series.[15]

Neither approach is rigorous so the discrepancies are not surprising. One may simply regard this as a defect of the $Z+1$ approximation. Alternatively, it follows from experience in the longer wavelength region (where many more than two members are resolved) that a larger quantum defect is required for the first member of the series than for the higher members.[16]

With the continuum located 15.75 eV above $K\beta_{1,3}$ the measurements of $K\alpha_1$ and $K\alpha_2$ may be used to infer the L_{III} and the L_{II} terms. The results are 248.43 eV for L_{III} and 250.61 eV for L_{II}. If the continuum location is valid, these should have standard deviations of about 0.05 eV. The mean term from Bagus's theoretical calculation,[17] 248.9 eV, appears to be satisfactorily near these values, but significantly removed from the empirical terms obtained by Bearden and Burr, viz., 245.2 and 247.3 eV with an assigned probable error of 0.3 eV.[11]

The origin of this discrepancy is not far to seek, since these authors have chosen to use energy positions of the first inflexion point of the absorption spectrum (which is probably appropriate in a metal) as the K-series term value in a situation where it is inappropriate. As is evident from Fig. 1, the K term lies approximately 3.1 eV above the "first inflexion" of the edge. Adding this to the K term of Bearden and Burr, namely, 3202.9 eV, gives a revised K term of 3206.0 eV. This combined with the experimental $K\alpha_{1,2}$, namely 2.95770 and 2.95563 eV, yields L_{III} terms of 248.3 and 250.4 eV, respectively. These are in quite satisfactory agreement with the values obtained in this work.

The present results on the L_{II} and L_{III} term values may also be compared with those deduced from photoelectron spectroscopy[18] and the x-ray L-series absorption spectra.[19, 20] Photoelectron spectroscopic values for the L_{II} and L_{III} terms have been obtained by Mehlhorn.[18] These results, viz., (250.53±0.25) and (248.39±0.25) eV are consistent with those obtained here and with L-series spectroscopic values (see below); they are, nevertheless, somewhat less precise.

The L_{III}-L_{II} region of the argon absorption spectrum as obtained by a single-crystal Bragg spectrometer, using an octadecyl hydrogen maleate crystal (OHM)[21] is shown in Fig. 2. Both origin of the energy scale and the limitations to its accuracy are noted in the Appendix. The profile is in substantial agreement with that reported by Lukirskii and Zimkina,[19] although the details are somewhat clearer in Fig. 2 than in the reference. This spectrum was interpreted in Ref. 19 by assigning the first two peaks to $2p \to 4s$ and $2p \to 5s + 3d$ while setting the L_{III}-L_{II} splitting the zero. This is not supportable in the light of the manifest 2.18-eV splitting of $K\alpha_{1,2}$, as shown in Fig. 1. The circumstance leading to the erroneous interpretation given in Ref. 19 is simply the close equality of the L_{II}-L_{III} interval with the expected separation of the $2p^{-1}\,4s$ and $2p^{-1}\,5s$ terms.

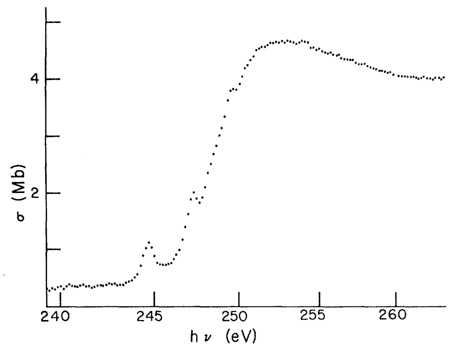

FIG. 2. L_{III}-L_{II} region of the argon absorption spectrum. These data were obtained with a single-crystal Bragg spectrometer using an OHM crystal. The energy scale was obtained from the diffraction equation using an effective grating constant at 50 Å obtained as described in the Appendix.

Very recent results produced by the Tokyo electron synchrotron group considerably improve the resolution and wavelength values for this spectrum.[20] The interpretation offered by those workers is in agreement with that suggested here, and is validated by the clear delineation of several members of each series. Their estimates of the L_{III}- and L_{II}-term energies agree with the estimates obtained above the K-series data within 0.1–0.2 eV.

V. CONCLUSION

It appears that any possible failure of the Ritz combination principle,[22] or level shifts due to configuration interaction,[23] are obscured by the uncertainty in locating the continuum. The remedy, if it is required, would be found in a better, and necessarily theoretical, estimate of the variation of the quantum defect in the Rydberg series at hand. It also appears that the spectroscopic quality of a Bragg-crystal instrument is substantially inferior to that of a grating spectrograph, at these wavelengths.

APPENDIX

The energy scale for Fig. 2 required an estimate of the effective grating spacing $2d$ for the OHM crystal used as dispersing element in a single-crystal Bragg arrangement of the vacuum, double-crystal instrument.[5]

Measurements of Cu$K\alpha_1$ in orders 8 and 11, combined with the chemistry $CH_3(CH_2)_{17}$–OOC–CH=CH–COOH and density (for index of refraction, assuming 200 active electrons/molecule) gave $2d = (63.344 \pm 0.005$ Å* for the first-order grating spacing.

An estimate of the effective spacing at 50 Å requires correction for the anomalous dispersion of the carbon K electrons. This was estimated from the universal dispersion curves given by James[24] (whose notation is followed). At 50 Å, $\omega/\omega K = 0.9$; from this and from an assumed K-shell oscillator strength of 1.8, $\Delta f'/g = 3.0$. This yields a correction of -120 electrons per molecule. The result is $2d_{\mathrm{eff}} = 63.215$ Å* (at 50 Å). The uncertainty is difficult to estimate but the value is probably no better than ±0.01 Å. This value was used to compute the energy scale in Fig. 2, using 12398.1 as the voltage wavelength-conversion factor.

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