error but are reproducible and, therefore, we assume are real.

Sweetman[5] has measured the cross sections for the reactions (a) $H_2^+ \to H+H$ (charge transfer) and (b) $H_2^+ \to H+H^+$ (dissociation) from 100 keV to higher energies. At 100 keV he finds cross sections of about 5×10^{-17} and 6×10^{-17} cm^2 for reactions (a) and (b), respectively. This means that 2.9, 0.5$_4$, 0.1% of the sum of reaction events (a) and (b) result in H_α, H_β, and H_γ emission, respectively. These fractions are considerably larger than the fraction of the corresponding Balmer emissions resulting from electron capture by protons in hydrogen.[1]

The H_3^+ impact curves exhibit a single broad maximum at about 50 keV. We assume that these curves are the result of mechanisms (6) and (7). (Afrosimov et al.[3] found that total charge transfer peaked at 40 keV for H_3^+ impact on H_2.)

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Multiple Excitation and Ionization of Inner Atomic Shells by X Rays*

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Reinvestigation of the region of the argon K absorption edge has revealed a new resonance absorption structure followed by a new continuum. These new features may be interpreted as arising from double-electron-excitation processes involving an M electron as well as the K electron. The first new resonance line lies about 22 eV above the first line in the previously observed single-electron-excitation resonance structure. No additional resonance structure was found in the region from zero to about 50 eV.

INTRODUCTION AND EXPERIMENT

THE x-ray absorption spectrum of gaseous argon in the region of the K edge (about 3.2 keV) has been reinvestigated with an automatic two-crystal vacuum spectrometer. A new absorption-edge structure was observed. This structure, interpreted as evidence for multiple-electron excitation and multiple ionization is discussed qualitatively in terms of a few particular two-electron transitions.

The details of the apparatus and techniques of two-crystal spectrometry have been presented elsewhere.[1] A few essentials are, however, pertinent in this discussion.

A platinum-plated copper anode served as the source of continuous x rays. The x-ray tube was operated at 14.3 kV and 54 mA. A pair of calcite crystals (having a parallel-position width of 10.1 sec of arc for $\lambda = 1.54$ Å radiation) was used. A gas cell 1.00-in. long with 0.001-in. beryllium windows and filled with research-grade argon was used as the absorber. The gas cell was filled to different pressures for the recording of different parts of the curve in Fig. 1. For the KM region of interest, the pressure was 213 mm Hg. The beam intensity with the gas cell evacuated (I_0) was 500 counts per sec. Intensity measurements for the region of interest were taken at intervals of 10 sec of arc (0.094 eV) by rotating the first crystal. A krypton-filled proportional counter was used to measure the intensity.

The absorption data, Fig. 1, represent the average of four complete passes through the wavelength region of interest. The ordinate values are in arbitrary absorption units proportional to $\ln(I_0/I)$, where I_0 is the incident and I is the transmitted intensity. The data have been corrected for instrumental effects such as background intensity and the several resolving power perturbations.[1,2] The resolving power correction does the following: (1) yields narrower lines and edges, (2) alters the degree of asymmetry, (3) enhances significantly the relative absorption contrast, and (4) shifts slightly the measured energy position of each structural component. Even though the spectral window is very narrow in this experiment ($\lambda/\Delta\lambda \approx 11\,000$), this correction is very important if detailed analysis is to be made of, or relative to, the K excitation.

[1] The apparatus and techniques used in this experiment are discussed in detail by H. W. Schnopper, Ph.D. thesis, 1962, Cornell University (to be published).

[2] L. G. Parratt, Rev. Mod. Phys. 31, 616 (1959); and J. O. Porteus, J. Appl. Phys. 33, 700 (1962).

FIG. 1. The extended argon K absorption edge showing only the corrected data.
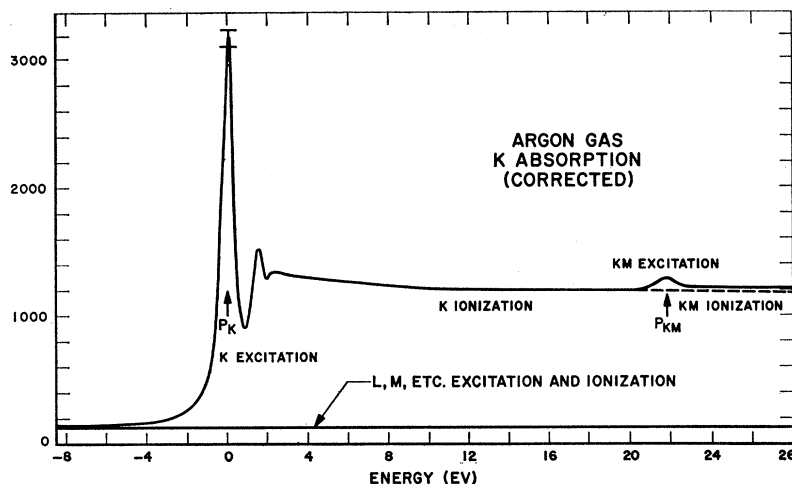
Before correction for resolving power, each measurement of absorption coefficient contains a statistical error (relative standard deviation) of no greater than one-half percent as determined from the total number of counts at each point. The statistical error of the points in the figure is somewhat greater than this because of the "jitter" inevitably introduced in unfolding the spectral window from the transmitted intensity data[1,2] (see Table I). The error bar in Fig. 1 refers to the corrected data.

TABLE I. Values of relative standard deviation in $\ln(I_0/I)$ at various energies. (See Fig. 1.)

| | Relative error | |
Energy (eV)	Uncorrected curve (%)	Corrected curve (%)
−6	1.90	5.7
0	0.59	1.7
6	0.34	1.0
18	0.46	1.0

RESULTS AND CONCLUSIONS

Five components of the curve are indicated: K excitation, K ionization, KM excitation, KM ionization, L, M, etc. excitation and ionization. The dashed line under the KM structure represents an extrapolation of the K ionization region. The zero of energy is arbitrarily chosen to be at the peak (P_K) of the first K excitation resonance line (about 3.2 keV). The peak (P_{KM}) of the first KM excitation resonance line is approximately 22 eV above P_K.

The K excitation and ionization parts of the spectrum have been previously observed and discussed.[3-7] The

series of resonance absorption lines labeled K excitation is believed to be due to single-electron transitions of the type $1s \rightarrow np$, where $n \geq 4$. The relatively smooth region, labeled K ionization, following this resonance line structure, is believed to represent electron transitions of the type $1s \rightarrow$ continuum.

The new structures, designated as KM excitation and KM ionization, are superposed on the K ionization region. The KM structures have all the features of another absorption "edge"—a resonance line structure followed by a continuum. It is proposed that both the new resonance and continuum structures are due to double-electron transitions resulting from the absorption of a single photon. The narrow resonance line together with the rather large transition probability are the features of current interest in the new structures.

The author is not aware of any pertinent theoretical work concerning the proposed photon induced double-electron transitions.[8] Possible transitions are the following:

(1) $\begin{cases} K \rightarrow M, N, O, P, \text{ etc. (bound final orbital) and} \\ M \rightarrow M, N, O, P, \text{ etc. (bound final orbital).} \end{cases}$

The KM continuum region following the resonance may arise from one or more of the following double-electron transitions:

(2) $\begin{cases} K \rightarrow M, N, O, P, \text{ etc. (bound final orbital) and} \\ M \rightarrow \text{continuum}; \end{cases}$

(3) $\begin{cases} K \rightarrow \text{continuum and} \\ M \rightarrow M, N, O, P, \text{ etc. (bound final orbital; and} \end{cases}$

(4) $\begin{cases} K \rightarrow \text{continuum and} \\ M \rightarrow \text{continuum.} \end{cases}$

These four sets of transitions, with further details

[3] D. Coster and J. H. van der Tuuk, Z. Physik 37, 367 (1926). These authors predicted but failed to find KM resonance structure.
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[6] G. Brogren, Nova Acta Regiae Soc. Sci. Upsaliensis 14, No. 4, (1948).
[7] T. Watanabe, Bull. Am. Phys. Soc. 7, 339 (1962).

[8] M. Wolfsberg and M. L. Perlman, Phys. Rev. 99, 1833 (1955), have, however, treated the case of multiple excitation in Auger processes.

specified, would provide a convenient starting point for calculations.

Final-state configurations in transitions of type (1) correspond to two different types of M holes. The first configuration contains an electron hole in both the K and the M_I shells, and the second contains a hole in both the K and the M_{II} or M_{III} shells. Transitions which result in these two final-state configurations should give rise to two resonance absorption structures appreciably different in energy position in the spectrum. The energy difference is given roughly by the $M_{II,III}$ to M_I separation in a hydrogenic atom, with the $M_{II,III}$ structure appearing at the lower energy. Theoretical evaluation of the energy separation $P_{KM} - P_K$ has not been made but, if P_{KM} refers to missing K and $M_{II,III}$ electrons, this energy separation should correspond roughly with the energy of the $M_{II,III}$ state in singly ionized potassium (which closely approximates an argon atom with a missing K electron). A first approximation to the relative intensity to be expected in the $KM_{II,III}$ and KM_I resonance structures is given by the ratio of the number of electrons in each shell, namely $(6/2) = 3$.

Since only one new resonance structure was, in fact, observed in the range 0 to 50 eV beyond the position of P_K, it seems plausible to assign this new structure, because of its energy position, to processes involving $M_{II,III}$ electrons. With this assignment, the absence of the KM_I resonance structure is perhaps reasonable on the basis of the intensity argument above—the KM_I structure would be barely above the experimental noise.

To recapitulate, a new structure has been observed in the K absorption spectrum of argon. This new structure is tentatively interpreted as arising from the simultaneous excitation of two electrons by an absorption of a single photon. The observations are particularly interesting since the physical system dealt with is a very simple experimental and theoretical case, namely, a monatomic, noninteracting atom.

ACKNOWLEDGMENTS

Proton Scattering by Molecules. I. The Two-State Oxygen Case and the Multistate Case*

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The inelastic scattering of protons by oxygen molecules is treated for the collision situation resulting in the excitation of the upper state of the Schumann-Runge system. The incident proton energy ranges from 1 to 50 keV. The total cross sections and the growth coefficient phases for this scattering are computed using the two-state impact-parameter treatment. The distortion of the molecular charge cloud by the incident proton is taken into account in the phase calculation. A method for multistate impact parameter treatment of the inelastic collision is developed, and the equations therefor are derived.

I. INTRODUCTION

HERE we consider the inelastic collision of protons with oxygen molecules resulting in the excitation of the Schumann-Runge system of oxygen. The proton energies range from 1 to 50 keV. The impact parameter treatment will be applied. This treatment was effectively introduced by Gurnee and Magee[1] in their study of charge transfer scattering. It has been discussed in connection with certain inelastic and charge transfer

hydrogen collisions by Bates[2] and somewhat improved upon by McCarroll.[3,4] The very slight differences between their treatment and ours seem to warrant a brief derivation.

In Sec. II the two-state impact-parameter formulation is discussed. In Sec. III the inelastic-scattering cross section for protons on oxygen molecules with the excitation of the Schumann-Runge system is calculated. In Sec. IV the phase of the initial-state growth coefficient is computed. For this computation

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