X-RAY SPECTRA FROM OXYGEN-ION BOMBARDMENTS ON Ca AND V AT 15 MeV†

D. Burch and Patrick Richard
University of Texas, Austin, Texas 78712
(Received 24 July 1970)

K x-ray spectra of Ca and V as produced by 15-MeV O^{4+} ion bombardment are compared with 6-MeV proton-induced spectra. The $K\alpha$ and $K\beta$ lines from the O^{4+} bombardment are found to be shifted approximately 54 and 157 eV, respectively, relative to the proton-induced spectra. Hartree-Fock-Slater calculations show that the observed shifts are on the order of those expected from atoms with two or three additional inner-shell vacancies. We argue that it is unlikely that the known low-energy ion-atom interactions could be responsible for such inner-shell ionization configurations.

The study of *K*-shell ionization by heavy ions has been limited, primarily, to incident-ion energies below approximately 3 MeV. At these low energies, the ion-atom interaction has been characterized by the formation of a quasimolecule, and extensive experimental data[1-3] and theoretical work[4-6] support this conclusion. Evidence is presented in this Letter that indicates that at much higher energies multiple inner-shell ionization may be taking place which results in an observable shift in the $K\alpha$ and $K\beta$ x-ray energies. The x-ray spectra of Ca and V were measured as produced by 6-MeV protons and 15-MeV oxygen 4+ ions. In these spectra the $K\alpha$ and $K\beta$ x rays from the oxygen bombardments are observed to shift to higher energies relative to the proton-induced x rays.

The experimental arrangement is as described in a previous paper where a shift in the $K\beta$ line was first reported.[7] 100-nA beams of the incident ions were produced by the University of Texas tandem Van de Graaff accelerator and focused onto rolled metal foil targets. X rays emitted from the target passed through a 0.5-mil Mylar window and were detected outside the vacuum system by a liquid-nitrogen–cooled Si(Li) nondispersive x-ray detector placed at 90° to the incident beam direction. The targets used were typically several mg/cm^2 thick, but the measurements were repeated in several cases with targets ~10^3 times thinner than these to rule out any possible target thickness effect. A proton spectrum was taken before and after each oxygen spectrum to check for any amplifier drift; and to prevent gain shift due to counting rate changes, all spectra were taken at counting rates of 500 counts/sec. Ca and V were studied with a system resolution of 180 eV (full width at half-maximum–FWHM) at 5.9 keV. Figure 1 contains the spectra for both proton and oxygen bombardments on both targets. The centroids of the peaks were located by fitting the data with a Gaussian plus background function. Energy calibrations were easily performed by proton bombardment on neighboring elements as the proton spectra were indistinguishable from the fluorescence spectra. The data were accumulated with equal counts in the $K\alpha$ line to point out that the $K\beta$ line is observed to broaden.

The results of the analysis of the data for Ca and V are summarized in Table I and the observed *K* x-ray energy shifts are given in Table II. The best-fit energies for the $K\alpha$ and $K\beta$ lines from the proton bombardments are consistent with the values tabulated by Bearden.[8] The resolution is 150 eV on the Ca $K\alpha$ line and 160 eV on the V $K\alpha$ line. Relative to the proton bombardments, the $K\alpha$ line produced by oxygen bombardments is shifted up 54 eV for Ca and 53 eV for V. The total error in these numbers is estimated to be ±6 eV. The $K\beta$ line shifts up 158 eV in Ca and 156 eV in V. Prior to the study of these two cases, all of the atoms from Ca to Zn were studied with a system having an energy resolu-

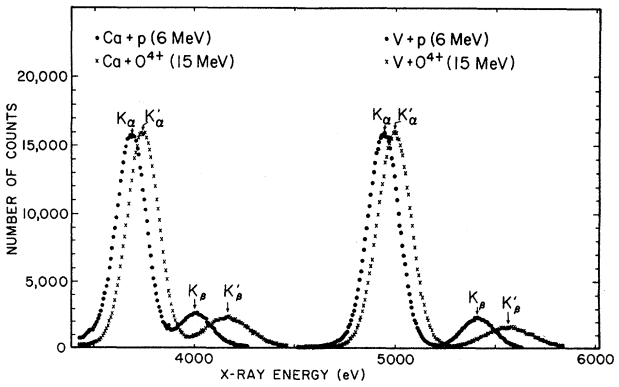

FIG. 1. X-ray spectra for Ca and V produced in proton and oxygen bombardments. The arrows below the symbols $K\alpha$ and $K\beta$ indicate the position of the centroids of the x-ray lines produced in the proton bombardments. The arrows below the symbols $K\alpha'$ and $K\beta'$ indicate the positions of the centroids for the oxygen bombardments.

Table I. X-ray data for Ca and V. Data taken with system resolution of 180 eV (full width at half-maximum at 5.90 keV). Energy calibration is based on best fit to proton-induced Ca and V x-ray energies assuming that the electronics is linear over the energy range 3.0 to 6.0 keV. Spectra were taken with 3.43 eV/channel.

	E_α^{exp} [a] (eV)	E_α^{Tables} [b] (eV)	Γ_α (eV)	E_β^{exp} (eV)	E_β^{Tables} (eV)	Γ_β (eV)
Ca+p (6 MeV)	3690±2	3690	150±3	4012±2	4013	184±10
Ca+O (15 MeV)	3744±1		159±3	4170±2		244±10
V+p (6 MeV)	4948±1	4948	160±3	5421±2	5427	173±10
V+O (15 MeV)	5001±1		170±3	5577±2		263±10

[a] The errors quoted here are fitting errors alone and do not include systematic errors.

[b] See Ref. 8.

tion of 280 eV at 5.9 keV. It was found that over this region the $K\beta$ shift is approximately constant at 140±25 eV while the $K\alpha$ shift is approximately 45±15 eV. The shifts referred to are relative to the x-ray energies as produced by proton bombardment.

An effect similar to the one described here has recently been observed in the L x-ray spectra of Ar^+-Ar collisions at much lower energies (50-330 keV).[3] In that work additional discrete lines are seen to appear and gain relative intensity while the original lines lose intensity as the incident argon energy is increased above 50 keV. The observed lines were interpreted as due to x rays from atoms with several outer electrons excited to higher levels via the level-crossing interaction as described by Fano and Lichten.[4]

However, in the present work, it is highly unlikely that a similar interaction and subsequent atomic configuration could result in the observed K energy shifts. More specifically, the calculations presented below indicate that the outermost three or four electrons can be removed completely with no observable effect on the $K\alpha$ or $K\beta$ energies. This result can also be seen for the $K\alpha$ energies of ions in the calculations of House.[9]

Secondly, the adiabatic approximations necessary in the quasimolecular model of Fano and Lichten are no longer valid at these energies: i.e., in the case of 100-keV Ar^+-Ar collisions, the nuclear velocities are 3 times smaller than those of the $M_{II,III}$-shell electrons whereas in the 15-MeV O^{4+} case, the nuclear velocities are 3 times larger than those of these outer-shell electrons.

Further evidence opposing the quasimolecular model is given by the measured total cross section for K-shell ionization by 15-MeV O^{4+} ions on Cu. This cross section corrected for the fluorescence yield (~26 b)[10] is 50 times smaller than predicted by a direct ion-electron interaction as calculated in the plane-wave Born approximation by Merzbacher et al.,[11,12] whereas in the energy region 20 keV to ~3 MeV the cross sections for K-shell ionization by heavy ions are several orders of magnitude greater than the predictions of the direct interaction model.[13] The level crossing during the formation of a transient quasimolecule allows for inner-shell ionization taking place at much larger ion-atom separation distances and hence the extreme rise in the cross section.

The Born approximation calculations, corrected for Coulomb deflection and K-electron binding to the projectile, do, however, predict accurately the K-shell ionization cross sections for incident protons with energies from 20 keV up to 28 MeV[14,15] and incident α particles up to 50 MeV.[16] This is consistent with the present data in that the K x-ray energies are independent of the incident proton energy, as expected, and that no such shift as reported here is observed in high-energy α bombardment.[17]

In order to get some idea as to the possible origin of the observed shifts, Hartree-Fock-

Table II. Ca and V x-ray energy shifts. $\Delta E_\alpha = E_\alpha(\text{oxygen}) - E_\alpha(\text{protons})$, $\Delta E_\beta = E_\beta(\text{oxygen}) - E_\beta(\text{protons})$. Data taken with system resolution of 150 eV for Ca $K\alpha$ and 160 eV for V $K\alpha$.

	ΔE_α (eV)	ΔE_β (eV)
Ca	54±6	158±6
V	52±6	156±6

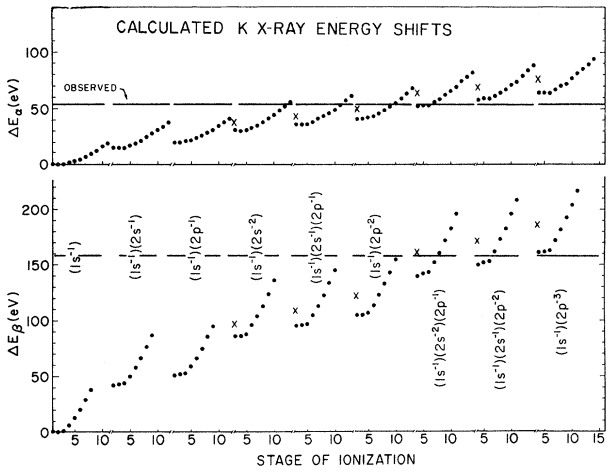

FIG. 2. Hartree-Fock-Slater calculations for the K x-ray energy shifts of various ion configurations. $\Delta E = E_K$(multiply ionized) $- E_K$(singly ionized) for both the $K\alpha$ and $K\beta$ energies. The labels $(1s)^{-1}(2p)^{-1}$, etc., refer to the core electrons removed from the neutral atom. The K x-ray energy for the decay of this ion is the first point of each series and is followed by points corresponding to the successive removal of the outermost available electron. The closed circles are the calculations for Ca, the x's are the calculations for the corresponding core excitations in V, and the solid horizontal lines are the experimentally observed shifts.

Slater calculations have been performed to estimate the expected shifts of the $K\alpha$ and $K\beta$ lines for multiply ionized atoms. Details of the calculations are given by Herman and Skillman,[18] with the x-ray energies defined as differences in total energy of the various ion states. These results for the case of Ca and V are given in Fig. 2. In that figure the label "$(1s)^{-1}(2s)^{-1}(2p)^{-1}$" identifies the expected x-ray energy for an atom with initial state $1s^1 2s^1 2p^5 3s^2 3p^6 4s^2$ and final state $1s^2 2s^1 2p^4 3s^2 3p^6 4s^2$, etc. Each "core excitation" of this type is then followed by the progressive removal of the outermost electrons. In the example above, the next calculation would be for initial state $(1s)^{-1}(2s)^{-1}(2p)^{-1}(4s)^{-1}$ followed by $(1s)^{-1}(2s)^{-1}(2s)^{-1}(4s)^{-2}$, etc. The last point in each of the series corresponds to leaving one p electron necessary for the K x-ray transition. The calculations for double K-shell ionization have not been included as they predict considerably larger energy shifts than observed.

The requirement of a simultaneous agreement for the $K\alpha$ and $K\beta$ shift provides a stringent test for the possible ionization state. It can be seen that the removal of two or three additional electrons from the L shell results in approximately the energies observed and that certain other ion configurations can be ruled out completely. The calculations indicate that the creation of several of the doubly and triply L-shell ionized atoms can produce a $K\beta$ line broadened by approximately 100 eV and a $K\alpha$ line broadened by approximately 50 eV. This is consistent with the oxygen bombardment data. A crystal spectrometer system with much higher energy resolution could possibly separate such components of the $K\beta$ line.

It should be noted that the calculations presented here provide only an estimate of the expected shift and that more rigorous calculations of this type are necessary to understand further the origin of such shifts.

If such selective inner-shell ionization is taking place, similar measurements of the L x-ray and KLL Auger electrons would provide additional criteria for determining the ion states produced. Furthermore, if the ion state can be determined then a comparison of calculated energies with the experimental energies could provide a measure of the correlation effects for specific electron shells.

---

†Work supported in part by the U. S. Atomic Energy Commission.

[1]M. E. Rudd, T. Jorgensen, and D. J. Volz, Phys. Rev. 151, 28 (1966).

[2] Q. C. Kessel and E. Everhart, Phys. Rev. 146, 16 (1966).

[3]M. E. Cunningham, R. C. Der, R. J. Fortner, T. M. Kavanagh, J. M. Khan, C. B. Layne, E. J. Zaharis, and J. D. Garcia, Phys. Rev. Lett. 24, 931 (1970).

[4]U. Fano and W. Lichten, Phys. Rev. Lett. 14, 627 (1965).

[5]W. Lichten, Phys. Rev. 164, 131 (1967).

[6]R. C. Der, R. J. Fortner, T. M. Kavanagh, and J. M. Khan, Phys. Rev. Lett. 24, 1272 (1970).

[7]P. Richard, I. L. Morgan, T. Furuta, and D. Burch, Phys. Rev. Lett. 23, 1009 (1969).

[8]J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967). The lines referred to loosely in the present paper as $K\alpha$ and $K\beta$ are actually multiplets of closely spaced lines which are given by Bearden and which are unresolved in the present experiment.

[9]L. L. House, Astrophys. J. Suppl. Ser. 18, 21 (1969).

[10]P. Richard, T. I. Bonner, T. Furuta, I. L. Morgan, and J. R. Rhodes, Phys. Rev. 81, 1044 (1970).

[11]E. Merzbacher and H. W. Lewis, *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1958), Vol. 34, p. 166.

[12]G. S. Khandelwal, B. H. Choi, and E. Merzbacher, At. Data 1, 103 (1969).

[13]W. Brandt and R. Laubert, Phys. Rev. Lett. 24, 1037 (1970).

[14]R. R. Hart, F. W. Reuter, III, H. P. Smith, Jr., and J. M. Khan, Phys. Rev. 179, 4 (1969); also see

detailed list of references in R. L. Watson, C. W. Lewis, and J. B. Natowitz, to be published.
[15]G. A. Bissinger, J. M. Joyce, E. J. Ludwig, W. S. McEver, and S. M. Shafroth, Phys. Rev. A 1, 841 (1970).
[16]Watson, Lewis, and Natowitz, Ref. 14.
[17]R. L. Watson, private communication.
[18]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

ANTI-STOKES RAMAN SCATTERING FROM METASTABLE DEUTERIUM ATOMS*

P. Bräunlich and P. Lambropoulos†
Bendix Research Laboratories, Bendix Center, Southfield, Michigan 48075
(Received 31 August 1970)

We have observed anti-Stokes Raman scattering from metastable deuterium atoms. The results obtained are in good agreement with theoretical calculations.

In a previous paper,[1] the observation of singly stimulated two-photon emission from the metastable $2s$ state of the deuterium atom was reported. In the presence of intense electromagnetic radiation of an optical frequency ω_{k_0}, another mode of decay of the metastable state is the emission of an anti-Stokes Raman photon. In this process, the metastable atom decays by absorbing an incident photon and emitting a photon of frequency $\omega_k = \omega_{2s} - \omega_{1s} + \omega_{k_0}$. If the incident radiation is unpolarized, the angular distribution of the emitted photons is given by $(1 + \cos^2\theta)$, where θ is the angle between the incident- and emitted-photon wave vectors $\vec{k}_0$ and $\vec{k}$, respectively. For deuterium metastables ($\hbar\omega_{2s} - \hbar\omega_{1s} = 10.19$ eV) and a Nd-glass laser ($\hbar\omega_{k_0} = 1.17$ eV), the wavelength of the Raman photon is $\lambda_k = 1090$ Å (or $\hbar\omega_k = 11.36$ eV) which is in the vacuum ultraviolet range of the spectrum.

The differential cross section for the emission of the Raman photon $\vec{k}$ within the solid angle $d\vec{\Omega}_{\vec{k}}$ is given by[2]

$$\frac{d\sigma}{d\vec{\Omega}_{\vec{k}}} = r_0^2 \frac{\omega_k}{\omega_{k_0}} \left(\frac{m}{\hbar}\right)^2 \left| \sum_6 \omega_k \omega_{k_0} \left[\frac{(\vec{r}_{1s,b} \vec{\epsilon}_{\vec{k}_0\lambda})(\vec{r}_{b,2s} \vec{\epsilon}_{\vec{k}\lambda})}{\omega_k + \omega_b - \omega_{2s}} + \frac{(\vec{r}_{1s,b} \vec{\epsilon}_{\vec{k}\lambda})(\vec{r}_{b,2s} \vec{\epsilon}_{\vec{k}_0\lambda})}{\omega_b - \omega_{2s} - \omega_{k_0}} \right] \right|^2, \quad (1)$$

where r_0 is the classical electron radius, m the electron mass, and $\vec{\epsilon}_{\vec{k}\lambda}$ the photon polarization vector. The symbol $\vec{r}_{1s,b}$ is an abbreviation for the matrix element $\langle 1s|\vec{r}|b\rangle$ and the sum is over all states of the atom. The presence of real states in resonance with the incident photon is not necessary for the process to occur.

If such resonant or near-resonant states do exist, however, the cross section is enhanced. In the present case, the incident photon was far from resonance with any of the intermediate states. For deuterium metastables and a Nd-glass laser, the cross section for the Raman process is about a factor of 6 larger than the cross section for singly stimulated two-photon emission.[2] However, experimental considerations subsequently discussed render its observation more difficult despite the larger cross section.

Assuming that the photon beam is essentially parallel, and denoting by I_0 its intensity (measured in number of photons per second), the number of uv photons emitted per laser shot within a small solid angle $\Delta\vec{\Omega}_{\vec{k}}$ is

$$R = I_0 \frac{d\sigma}{d\vec{\Omega}_{\vec{k}}} \Delta\vec{\Omega}_{\vec{k}} N l t, \quad (2)$$

where N is the number of metastables per unit volume in the interaction area, l the length of the interaction area along the laser beam, and t the duration of the laser pulse.

If, in addition to the photons ω_{k_0}, photons of frequency $\omega_k = \omega_{2s} - \omega_{1s} + \omega_{k_0}$ are present in the initial state, then the stimulated anti-Stokes Raman emission becomes possible. This process is proportional to the product of the intensities of the two frequencies, and the emitted photon is identical to, and in phase with, the incident uv photon. Provided that certain experimental conditions can be realized, it is conceivable that one may be able to use a single laser beam to generate enough anti-Stokes photons to trigger the stimulated emission. Such processes could be very valuable for the creation of coherent vacuum ultraviolet radiation.