Mo K and U L X-Ray Transitions from Separated Isotopes

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The $K\alpha(K\rightarrow L_{III}, K\rightarrow L_{II})$ x-ray lines of Mo and the $L\beta_1(L_{II}\rightarrow M_{IV})$ and $L\alpha_1(L_{III}\rightarrow M_V)$ x-ray lines of U have been measured from separated isotopes using a double-crystal x-ray spectrometer. The x-ray transitions were induced by radiative excitation from a W target x-ray tube. Intensities were measured with a 70-cm Kr-filled Geiger counter.

No evidence of nuclear isotopic effects (hyperfine structure and isotope shift) on the x-ray levels was found in the measurement of these transitions. The $K\alpha$ transitions from the separated isotopes Mo^{92} (95.5 percent), Mo^{95} (88.0 percent), and Mo^{100} (86.65 percent) in MoO_3 and the $L\beta_1$ and $L\alpha_1$ transitions from the separated isotopes of U^{235} and U^{238} in U_3O_8 show no measurable shift in peak positions and no changes in line widths. The limit of an observable effect is 0.2 volt for the Mo transitions and 0.4 volt for the U transitions.

I. INTRODUCTION

THE high resolution available in optical spectroscopy has revealed in the spectra of many isotopes a hyperfine structure and an isotope shift. The hyperfine structure can essentially be understood by attributing to the nucleus an angular momentum I and a magnetic moment μ. The isotope shift for heavy elements results from a nuclear "volume" effect.[1] In many cases, values of nuclear moments and information on nuclear charge distribution have been obtained from spectroscopic studies. McNally[2] has pointed out the advantages of using separated isotopes for this work.

Some years ago Breit[3] considered the possible effects of nuclear spin and magnetic moment on x-ray levels, and he showed that they might cause small but presumably measurable separations of x-ray terms. Breit suggested the use of the double-crystal x-ray spectrometer for possible detection of this effect.

This suggestion of Breit was investigated by Richtmyer and Barnes[4] and by Williams[5] without success. Richtmyer and Barnes examined the $K\alpha_1$ line of W with the double crystal spectrometer and found no evidence of a hyperfine structure. Williams also used the double crystal spectrometer in a study of the width of twelve lines in the U L series. In his experiments he found no evidence for the splitting of the L levels. He suggested that the large natural width of the lines would prevent observation of hyperfine structure.

It should be pointed out that the isotopic abundances in normal U and W are not favorable for experimental detection of an x-ray hyperfine structure. W contains about 86 percent even-mass-number isotopes. The one odd-mass-number isotope of W has a nuclear spin of $\frac{1}{2}$ and a magnetic moment of only 0.09. Normal U consists of about 99.3 percent U^{238} and 0.7 percent U^{235}. Thus the measurements on W by Richtmyer and Barnes and on U by Williams depended largely on even-even nuclei for which $I=0$ and $\mu=0$.

Frilley, Gokhale, and Valadarès,[6] in an experimental attempt to observe x-ray hyperfine structure, measured the widths of the $K\alpha$ lines from $_{37}$Rb to $_{50}$Sn. Because of the high spin and magnetic moment of Nb and the two In isotopes, a measurable hyperfine broadening of the $K\alpha$ lines from these two elements was expected. However, their measurements showed no departures in these line widths from the normal variation of the line widths as a function of Z indicating no hyperfine structure. Curie[7] has discussed the results of Frilley, Gokhale, and Valadarès and has given a possible explanation of these results.

As found in optical spectroscopy, one should also expect an x-ray isotopic shift from the nuclear "volume" effect. Such an effect has also not yet been observed. Detailed calculations of this shift have been made for the optical levels but appear to be lacking for the x-ray levels. The smallness of the effect can perhaps be inferred from some calculations of Brenner and Brown[8] on K binding energies of heavy elements. They found that if the nucleus instead of being a point charge is a charged spherical shell of radius $r_0\sim 5e^2/mc^2$, then the change in the binding energy of a K electron is of the order of $Z^4\alpha^6mc^2$, which is about 0.1 Rydberg for mercury. This nuclear "volume" effect depends on the distribution of nuclear charge and should increase for an ellipsoidal shape, assuming the same volume. Large optical shifts have been measured for isotopes having a high electric quadrupole moment. The use of selected separated isotopes, now available, suggests itself for a critical study of hyperfine structure and isotope shift of x-ray levels.

In recent work, Brown[9] has reported the measurement of x-ray transitions as a result of radioactive decay

[1] J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932); M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).
[2] J. R. McNally, Jr., Am. J. Phys. **20**, 152 (1952).
[3] G. Breit, Phys. Rev. **35**, 1447 (1930).
[4] F. K. Richtmyer and S. W. Barnes, Phys. Rev. **37**, 1695 (1931).
[5] John H. Williams, Phys. Rev. **37**, 1431 (1931).
[6] Frilley, Gokhale, and Valadarès, Compt. rend. **233**, 1183 (1951).
[7] Daniel Curie, J. Phys. et radium **13**, 505 (1952).
[8] S. Brenner and G. E. Brown, Proc. Roy. Soc. (London) **A218**, 422 (1953).
[9] Charles I. Brown, Jr., University of California Radiation Laboratory Report UCRL-1764 (unpublished).

using a ten-inch bent-crystal spectrometer. He reports an apparent anomaly in the energies of the U L x-rays emitted after the β decay of Pa^{232} and Pa^{233}, the x-ray energies being uniformly higher by as much as 50 volts than the energies of the U L lines emitted after the decay of Pu^{239} or those reported by Siegbahn from conventional x-ray excitation. No explanation for this apparent effect was advanced.

We have started a program searching experimentally for x-ray isotopic effects (hyperfine structure and isotope shift) by measuring corresponding transitions from highly enriched separated isotopes. We have so far examined the $K\alpha_1$ and the $K\alpha_2$ transitions from electromagnetically enriched Mo^{92}, Mo^{95}, and Mo^{100} [10] and the $L\beta_1$ and the $L\alpha_1$ transitions from separated isotopes of U^{235} and U^{238}.[11]

II. EXPERIMENTAL

We have employed the standard techniques of double-crystal x-ray spectroscopy in the measurement of the x-ray transitions. However, the value of the enriched separated isotopes demanded a technique which would result in no loss or contamination of the samples. For this reason the transitions were not produced by electron bombardment but rather by radiative excitation.

W x-ray radiation was produced from a Machlett A-2 tube at 40 kv and 20 ma. The voltage supplied to the tube and the x-ray tube current were both stabilized to within 0.1 percent. The isotopic compound was placed in a specially constructed brass holder shown in Fig. 1. The cavity containing the material measured 4 mm×8 mm and was $\frac{1}{2}$ mm deep. The compound was covered with a thin aluminum foil (0.0005 in.) which was secured to the holder with a metal frame. The 8-mm dimension of the cavity was inclined at a 30° angle with the horizontal. The isotope holder could be removed for sample change and precisely repositioned by sliding in grooved runways. The x-ray tube was clamped in a horizontal position with the tube window immediately above the isotope holder. The exciting radiation emerged downward, striking the compound and producing fluorescent radiation. The x-ray tube base and isotope holder were enclosed in a lead box to confine scattered radiation.

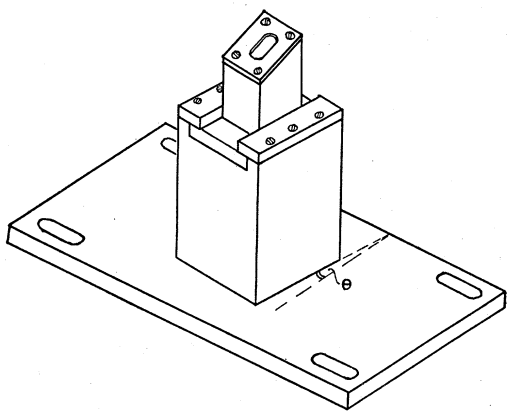

FIG. 1. Sample holder.

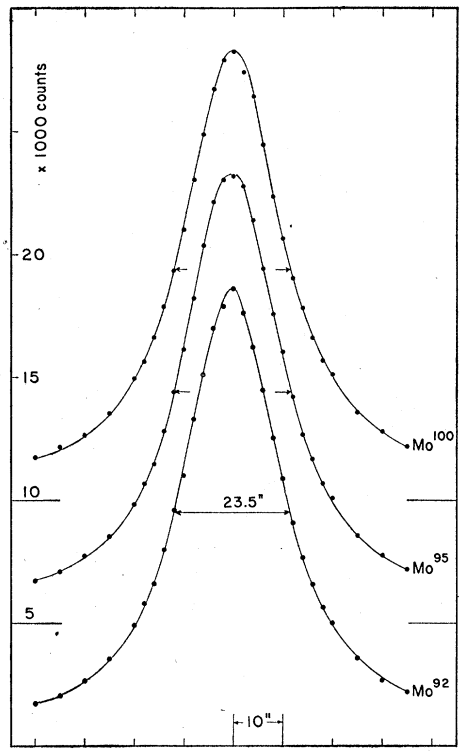

FIG. 2. Mo$K\alpha_1$ lines from Mo^{92}, Mo^{95}, and Mo^{100}. The zero line for the Mo^{95} curve is at 5000 counts, for the Mo^{100} curve at 10 000 counts.

An opening in the front of the lead box permitted the fluorescent radiation to pass through a slit system and strike the first crystal of a double-crystal spectrometer. Diffracted radiation in turn passed to the second crystal and finally entered a Geiger counter filled with krypton to a pressure of 70 cm. Data on the x-ray lines were recorded by counting for fixed time intervals, either one or two minutes, point by point through the line. Numerous runs were obtained, resetting the spectrometer and counting over at the same points.

A search for isotopic effects necessitates the highest resolution available. For the double-crystal spectrometer the physical resolving power which limits the available resolution is dependent on the crystal perfection. The calcite crystals of our spectrometer have been in use for about two years and consistently give line widths that indicate that these crystals compare favorably with the best crystals reported. The spectrometer is of the Ross type having a translating first crystal and a rotating second crystal. The rotation of the second

[10] Obtained on U. S. Atomic Energy Commission approved loan from Stable Isotope Research and Production Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[11] Obtained on loan through contract with the U. S. Atomic Energy Commission.

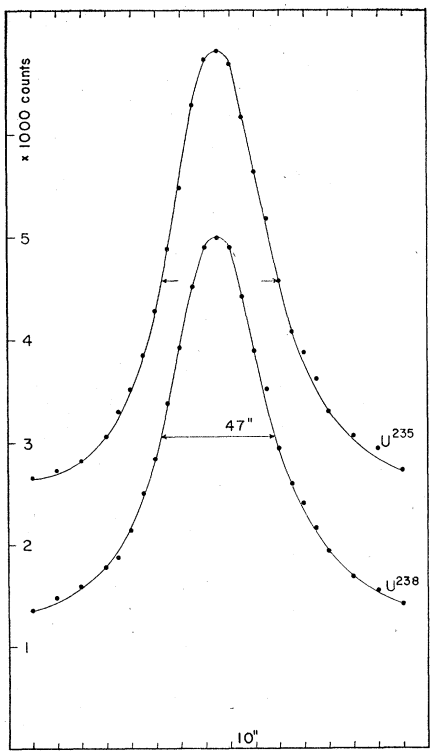

FIG. 3. U $L\beta_1$ lines from U^{235} and U^{238}. The zero line for the U^{235} curve is at 1200 counts.

crystal is performed by means of a precision micrometer screw and a lever arrangement. The micrometer head is engraved with 200 divisions, each division corresponding very closely to a crystal rotation of 1″. Absolute angles cannot be measured with this spectrometer, but angular differences are measured to better than 1″. The micrometer has been calibrated by measuring the angular difference between peaks of the $K\alpha_1$ and $K\alpha_2$ lines for Mo.

III

A. Results—Mo

The K x-ray lines of molybdenum have been measured by numerous investigators, among them Allison and Williams.[12] The $K\alpha$ lines have been found to be highly symmetrical and the lowest half-width value in the (1, +1) position has been reported to be 21″ for $K\alpha_1$. Our spectrometer gives a half-width value of 23.5″.

The separated Mo isotopes were in the chemical form MoO_3. The $K\alpha_1$ line shown in Fig. 2 was measured for normal MoO_3, $Mo^{92}O_3$, $Mo^{95}O_3$, and $Mo^{100}O_3$. Table I gives the isotopic abundance of the various samples. Five runs were made for each sample with a total peak count of about 18 000 counts for each. We find no measurable differences for this transition from separated isotopes. The peak positions and half widths for all samples agree to within 0.5″. Since the dispersion at this wavelength is close to 3″/volt, it can be stated that any existing isotopic effect on the K-transitions for Mo is less than 0.2 volt.

As a check, we have also measured the $K\alpha_2$ transition from the separated isotopes, and again we find no measurable effects on half-width or peak position. Thus, no influence on the $K\alpha$ x-ray transitions of Mo isotopes has been found either for the nuclear spin of Mo^{95} or for the nuclear "volume" difference of Mo^{92}, Mo^{95}, and Mo^{100}.

B. Results—U

The U $L\beta_1$ line which represents a transition from the $L_{II} \rightarrow M_{IV}$ state was measured from separated isotopes of U^{235} and U^{238} in the form of U_3O_8. Since the fluorescent intensity of the U L lines is much lower than that of the Mo K lines under the same excitation conditions, more runs were taken. As a further check, the line was measured twice changing the sample each time. In one case 12 runs were taken accumulating 4800 counts at the peak, and in the other case 10 runs were taken with a total peak count of 8000 counts, both for U^{235} and U^{238}. The results again indicate no measurable differences. The greater width of this line, measured to be 47″, raises the limit of an observable effect to about 1″ or 0.4 volt. The peak positions and line widths agree to within this limit.

TABLE I. Mo isotope mass analysis (in atom percent).

	92	94	95	96	97	98	100
Mo^{92}	95.5	0.8	0.8	0.8	0.4	1.3	0.5
Mo^{95}	1.1	2.2	88.0	4.2	1.2	2.7	0.7
Mo^{100}	1.70	2.02	1.93	2.35	1.32	4.04	86.65
Mo (normal)	15.86	9.12	15.7	16.5	9.45	23.75	9.62

The $L\alpha_1$ line from U^{235} and U^{238}, a $L_{III} \rightarrow M_V$ transition, has also been measured, showing no measurable difference in the x-ray transitions from the separated isotopes.

L lines originating from the L_I level are more difficult to excite and are too weak to measure with our experimental arrangement. The closeness of the U $L\beta_1$ line to the Mo $K\alpha$ lines allowed us to make a precision measurement of its wavelength with respect to the Mo $K\alpha$ doublet. We find that the angular difference between Mo $K\alpha_1$ and U $L\beta_1$ agrees to within 1″ with that calculated from the wavelength values given in the tables of Cauchois and Hulubei.[13]

IV. CONCLUSIONS

No measurable isotopic effects have been observed for the $K\alpha$ x-ray transitions of Mo^{92}, Mo^{95}, and Mo^{100} in MoO_3. The double-crystal technique would have

[12] S. K. Allison and J. H. Williams, Phys. Rev. **35**, 1476 (1930).

[13] Y. Cauchois and H. Hulubei, *Longuers d'ondes des émissions X et des discontinuités d'absorption X* (Hermann and Company, Paris, 1947).

shown differences of 0.2 volt for these lines. Similarly no measurable differences were found for the $L\alpha_1$ and $L\beta_1$ lines from U^{235} and U^{238} in U_3O_8. The increased width of these lines raises the limit of an observable effect to 0.4 volt. It appears that present x-ray spectroscopic techniques lack the resolution to detect nuclear isotopic influences on these x-ray levels. However, it may still be possible that somewhere in the isotopic chart a radical change in nuclear "volume," for example, may yet allow a measurable x-ray isotopic effect. It also appears of interest to make precision wavelength measurements of x-rays emitted in radioactive decay to see whether their energies really differ from x-rays produced in the conventional manner.

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One-to-Two Millimeter Wave Spectroscopy. III. NO and DI†

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Pure rotational transitions of $N^{14}O^{16}$ and DI^{127} have been measured in the one-to-two millimeter wave region. For NO the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition in the $^2\pi_{\frac{1}{2}}$ electronic ground state was observed. The transition reveals a Λ doublet with separation $\Delta\nu_{dc}=355.1$ Mc/sec. Each component of the Λ doublet is further split into five hyperfine components as a result of the nuclear magnetic coupling of N^{14}. Nuclear quadrupole coupling of N^{14} was found to be small in comparison with the magnetic interaction. Analysis of the data yields $B_0=50818.0$ Mc/sec, $r_0=1.1540$ A, $B_e=51084.8$ Mc/sec, and $r_e=1.1510$ A for the $^2\Pi_{\frac{1}{2}}$ state. For DI^{127} the following information was obtained: $B_0=97\ 537.2$ Mc/sec, $r_0=1.6165$ A, and $eQq(I^{127})=1823\pm1$ Mc/sec. Nuclear magnetic interactions of I^{127} were also detected and analyzed.

INTRODUCTION

THE opening up of the one-to-two millimeter wave region[1] has made it possible to study with the high precision of microwave methods the pure rotational spectra of such light diatomic molecules as NO and the deuterium halides, which, because of their small moments of inertia, were previously inaccessible to microwave spectroscopists. Results on NO and DI are reported here. We are searching for the lines of DBr and hope to measure DCl also.

NITRIC OXIDE

The electronic ground state of NO is $^2\Pi_{\frac{1}{2}}$, but only 120 cm^{-1} above lies the $^2\Pi_{\frac{3}{2}}$ state, also appreciably populated at room temperature. We have investigated the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ rotational transition of molecules in the $^2\Pi_{\frac{1}{2}}$ state. Because of the cancellation of the orbital and spin magnetic moments the $^2\Pi_{\frac{1}{2}}$ state is supposedly nonmagnetic. Nevertheless, widely spaced magnetic hyperfine structure was found. Table I gives the pattern of 10 lines which were observed. Figure 1 shows the lower frequency group of five as they appeared on the cathode-ray scope.

Without nuclear interaction the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition would be expected to have two components because of Λ doubling. Nuclear interaction with N^{14} would split each component of the doublet into five components, as observed. Each hyperfine multiple was found to fit an equation of the form

$$E=P\{F(F+1)-J(J+1)-I(I+1)\}+R\{(3/4)C(C+1)-J(J+1)I(I+1)\},$$

with $C=F(F+1)-J(J+1)-I(I+1)$, derived by Dr.

TABLE I. Observed and calculated components of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition, $^2\pi_{\frac{1}{2}}$ state, of $N^{14}O^{16}$.

Transition $F\rightarrow F'$	Frequency (Mc/sec) Observed	Calculated[a]	Relative intensity Observed	Calculated
Lower frequency group of Λ doublet $\nu_0{}^c=150\,195.49$ Mc/sec				
$\frac{3}{2}\rightarrow5/2$	150,176.54	150,176.52	100	100
$\frac{1}{2}\rightarrow\frac{3}{2}$	150,198.85	150,198.85	35	37.1
$\frac{3}{2}\rightarrow\frac{3}{2}$	150,218.89	150,218.89	30	29.6
$\frac{1}{2}\rightarrow\frac{1}{2}$	150,225.75	150,225.80	30	29.6
$\frac{3}{2}\rightarrow\frac{1}{2}$	150,245.69	150,245.70	5	3.7
Upper frequency group of Λ doublet $\nu_0{}^d=150\,550.60$ Mc/sec				
$\frac{3}{2}\rightarrow\frac{1}{2}$	150,375.48	150,375.47	5	3.7
$\frac{3}{2}\rightarrow\frac{3}{2}$	150,439.22	150,439.21	30	29.6
$\frac{3}{2}\rightarrow5/2$	150,546.50	150,546.46	100	100
$\frac{1}{2}\rightarrow\frac{1}{2}$	150,580.70	150,580.64	30	29.6
$\frac{1}{2}\rightarrow\frac{3}{2}$	150,644.37	150,644.32	40	37.7

[a] See reference 2.

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* Shell Oil Company Fellow.
[1] W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953).