## Identification of Two Radioactive Xenons from Uranium Fission

The observation of two long-life radioactive xenons growing out of radioactive iodine from uranium fission has been reported by us[1] and confirmed by Dodson and Fowler.[2] Recently some samples of cesium and barium were placed immediately behind a beryllium target bombarded by 16-Mev deuterons. After the bombardment the active cesium or barium was dissolved in water and the radioactive gas was then extracted into an ionization chamber. In the case of cesium only one radioactivity was observed which decayed with a half-life of 5 days, but in the case of barium, both 9.4-hr. and 5-day periods were present. The identity of the periods and of the absorption curves of these 9.4-hr. and 5-day radioactive gases from cesium and barium with those of radioactive xenon from uranium and thorium fission proves that they are the same substances.

Cesium has only one stable isotope with a mass number of 133, and since its bombardment gives only one radioactive xenon, we assume that the 5-day xenon is produced by the following reaction

$$_{55}Cs^{133}(n, p)_{54}Xe^{133}$$
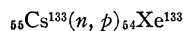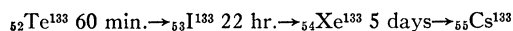
and assign to it the mass number 133.

Although barium has seven known isotopes (130, 132, 134, 135, 136, 137 and 138), only three of them would be able to produce radioactive xenon (except for isomers of stable nuclei) by $a(n, \alpha)$ reaction. These are 130, 136, and 138. We have seen that Ba gives by $a(n, \alpha)$ reaction the 5-day xenon and we interpret this as
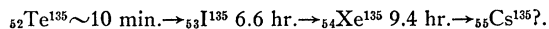
$$_{56}Ba^{136}(n, \alpha)_{54}Xe^{133}.$$
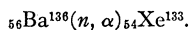
Since the abundance of Ba^{130} is only 1/700 of that of Ba^{138}, it is very likely that the barium of mass number 138 is responsible for the formation of the 9.4-hour xenon according to the reaction

$$_{56}Ba^{138}(n, \alpha)_{54}Xe^{135}.$$
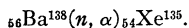
Based on these results, the two chains found in uranium and thorium fission may be identified as

$$_{52}Te^{133} \text{ 60 min.} \rightarrow _{53}I^{133} \text{ 22 hr.} \rightarrow _{54}Xe^{133} \text{ 5 days} \rightarrow _{55}Cs^{133}$$

and

$$_{52}Te^{135} \sim 10 \text{ min.} \rightarrow _{53}I^{135} \text{ 6.6 hr.} \rightarrow _{54}Xe^{135} \text{ 9.4 hr.} \rightarrow _{55}Cs^{135}?.$$

Iodine was also separated from the fast-neutron-activated cesium sample. The separated iodine decayed with a single period of 12.6 hr. This confirms the assignment[3] of 12.6-hr. iodine to $_{53}I^{130}$ resulting from a reaction

$$_{55}Cs^{133}(n, \alpha)_{53}I^{130}.$$
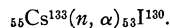
The author wishes to thank Professor E. O. Lawrence for his interest in this work and Dr. E. Segrè for his helpful suggestions and criticisms.

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October 17, 1940.

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Vibration Analysis of the Chlorine Dioxide Absorption Spectrum

The electronic band system appearing in the absorption spectrum of chlorine dioxide between 2600A and 5225A has been measured by several investigators[1-4] and vibration analyses have been attempted. The author offers evidence in support of a new analysis. Urey and Johnston were the first to attempt a detailed analysis of this system. However, none of their frequencies for the ground state agreed with the two infra-red frequencies found later by Bailey and Cassie;[5] namely, 945 cm^{-1} and 1109 cm^{-1}. For the third fundamental frequency of the ground state Bailey and Cassie accepted 528 cm^{-1} which appeared as a constant difference in two pairs of strong progressions in Urey and Johnston's analysis. Later Ku made more accurate and more complete measurements on the bands and attempted an analysis using the above frequencies but did not use the selection rules of Herzberg and Teller.[6]

Using the data of Ku, one finds that the 528 frequency comes out to be either 528 cm^{-1} or 524 cm^{-1} depending on which pair of progressions is used in determining its value. This disagreement is greater than experimental error. The author proposes to replace the fundamental frequency of 528 cm^{-1} by 447 cm^{-1} which appears as a constant difference in three separate pairs of progressions.

Photographs taken by the writer with the absorbing gas at dry ice temperature give clear evidence in support of this change.

From electron diffraction experiments, Brockway[7] finds that the apex angle of ClO_2 is 137°±15°. On this basis one must make the following assignment to the fundamental frequencies of the lower state:

$$\nu_1'' = 447 \text{ cm}^{-1},$$
$$\nu_2'' = 945 \text{ cm}^{-1},$$
$$\nu_3'' = 1109 \text{ cm}^{-1},$$

where ν_1'' designates the frequency of the bending vibration, ν_2'' that of the breathing vibration, and ν_3'' that of the antisymmetrical vibration. The apex angle of the lower state of ClO_2 calculated from these frequencies on the basis of the valence force model is approximately 122°.

As for the symmetrical frequencies of the upper state, the author essentially agrees with Urey and Johnston as well as Ku. These are:

$$\left. \begin{array}{c} \nu_1' \\ \nu_2' \end{array} \right\} \begin{cases} 290 \text{ cm}^{-1}, \\ 708 \text{ cm}^{-1}. \end{cases}$$

The bands have been photographed by the writer in the second order of the 30-ft. 30,000-line per inch grating at the University of Chicago. Each band is made up of sub-bands, some of which show clearly defined rotational series. This rotational structure is now in process of analysis. The sub-bands, like the bands themselves, degrade to the red. This is sufficient to show that both dimensions of the molecule increase as it passes to the upper state.

Further, the 708 frequency is excited up to 20 quanta or more, while no more than two quanta of the 290 frequency are excited with enough intensity to be observed. If qualitative use is made of the Franck-Condon principle,

the foregoing facts require the assignment

$$\nu_1' = 290 \text{ cm}^{-1},$$
$$\nu_2' = 708 \text{ cm}^{-1}.$$

In addition, if use is made of two series in which it appears that ν_3' changes by two quanta, the present analysis gives

$$\nu_3' = 790 \text{ cm}^{-1}.$$

On the basis of these approximate frequencies, the angle for the upper state is found to be about 114° compared to 122° in the lower state. This small change is consistent with the already mentioned fact that only ν_2' progressions are appreciably excited. The numerical value of each frequency given above corresponds to a one-quantum jump from the 0, 0, 0 state of vibration.

All distinct bands excluding isotope bands are now grouped into twelve progressions. All other reported bands can be classed as sub-bands, or are in the violet region of the spectrum where predissociation causes confusion. In the notation $(\nu_1'\nu_2'\nu_3') \leftarrow (\nu_1''\nu_2''\nu_3'')$ these progressions are:

STRONG	MEDIUM
$(0\ \nu_2'\ 0) \leftarrow (0\ 0\ 0)$	$(0\ \nu_2'\ 0) \leftarrow (0\ 1\ 0)$
$(1\ \nu_2'\ 0)$	$(1\ \nu_2'\ 0)$
$(0\ \nu_2'\ 2)$	
$(1\ \nu_2'\ 2)$	WEAK
	$(0\ \nu_2'\ 0) \leftarrow (0\ 2\ 0)$
MEDIUM	$(1\ \nu_2'\ 0)$
$(0\ \nu_2'\ 0) \leftarrow (1\ 0\ 0)$	
$(1\ \nu_2'\ 0)$	WEAK
$(2\ \nu_2'\ 0)$	$(0\ \nu_2'\ 0) \leftarrow (1\ 1\ 0)$

The $(0\ 0\ 0) \leftarrow (0\ 0\ 0)$ band, contrary to previous analysis, is the 21,016 cm^{-1} band.

The fact that $(0\ \nu_2'\ 2) \leftarrow (0\ 0\ 0)$ and $(0\ \nu_2'\ 0) \leftarrow (0\ 1\ 0)$, as well as $(0\ \nu_2'\ 0) \leftarrow (0\ 2\ 0)$ are stronger than would ordinarily be expected is consistent with the qualitative picture of the Franck-Condon principle, taking into consideration the change in shape of the molecule.

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Chicago, Illinois,
October 25, 1940.

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Remarks on the Temperature Dependence of the Work Function of Tungsten

A few remarks in criticism of the paper by J. G. Potter[1] on "Temperature dependence of the work function of tungsten . . ." are called for, since in my opinion Dr. Potter has overestimated the reliability of the interpretation of his work when he writes: "The coefficient obtained resolves the discrepancy between the experimental value of A in the Richardson equation and the theoretical factor of 120 without the introduction of a reflection coefficient."

The so-called "experimental" value of A is taken as 60 amp. per sq. cm per degree squared. Its determination depended on the assumption that the entire area of the filament studied had a constant work function and that this could be obtained by measuring the emission with a strong accelerating field and then extrapolating back according to the Schottky theory to zero in order to evaluate the "theoretical" emission which should obtain at zero field.

Experiments by Johnson and Shockley,[2] Martin,[3] and Nichols[4] demonstrate beyond any doubt that the emission from a tungsten wire is far from uniform and, in fact, probably over 95 percent of all of the emission comes from less than 50 percent of the surface. Although no theoretical investigation has as yet shown that an appreciable reflection effect is to be expected when very slow electrons pass over a potential barrier, *all* experiments designed to investigate the energy distribution of electrons emitted thermionically or photoelectrically show a very considerable deficiency in the number of slow electrons. The experimental fact is that the order of 50 percent or more of the electrons normally expected are apparently reflected at the surface and do not contribute to the observed emission. Either the effect of the non-uniform emission or the reflection effect alone would be capable of "resolving" the discrepancy between the "experimental" value of $A = 60$ and the theoretical value of $A = 120$. A positive temperature coefficient of the work function as reported by Dr. Potter makes matters worse when all of the recognized experimental results are considered.

The negative temperature coefficient of the work-function as determined by Langmuir[5] has been shown[6] to be capable of resolving the difficulty and yet it is necessary to stress the fact that this problem cannot be said to be "resolved" until every step in the argument has been checked and cross-checked by independent experiments since the experimental difficulties are known to be so great.

Dr. Potter leads the reader to think that Langmuir attributed his observed negative temperature to "effects resulting from imperfect vacuum conditions." A careful reading of Langmuir's paper shows that the more likely source of error was to be attributed to possible alterations in the exact relative positions of his tube elements as the temperature was changed. As a result of a recently completed investigation of field emission by J. H. Daniel,[7] it has been possible to demonstrate that even under the most favorable vacuum conditions, which can be obtained only with sealed-off and properly "gettered" tubes, a surface of tungsten cannot be maintained at temperatures below 900°K more than a very few minutes without considerable alteration of the work function because of the adsorption of gas. Most experimenters in this field know that serious adsorption takes place many times more rapidly when the experimental tube is *not* sealed off from the pumping system even though the pressure as measured by an ionization gauge is of the order of 5×10^{-9} mm. Therefore it is not surprising that Dr. Potter experienced so much difficulty in this respect. At this pressure a monolayer could be formed in about five minutes and only a fraction of a monolayer is needed to make a very considerable alteration in the work function. This would confuse any measurements