

## Vibrational Fine Structure in the Absorption Spectra of Uranyl and Plutonyl Ions in Aqueous Solution

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The value of  $L_s$  is

$$L_s = [l! / (\prod_k (k!)^{n_k} n_k!)], \quad (5)$$

since the permutation between the molecules within each more-than-singly connected cluster and the permutation between clusters of identical number of molecules do not lead to new arrangements.

To find  $M_s$ , we notice that there are always  $n-1$  molecules common to  $n$  more-than-singly connected clusters. If a molecule joins up  $p$  clusters, it is counted as  $p-1$  molecules. Thus in Fig. 1,  $n=4$  and  $n-1=3$ , namely, molecules 6, 7, and 8. In Fig. 2,  $n=5$  and  $n-1=4$ , namely, molecules 5, 10, and 14, molecule 5 being considered as two molecules since it connects up three clusters. Since there are  $n-1$  molecules common to the more-than-singly connected clusters and since the singly connected cluster can be formed by putting in any one of the  $l$  molecules, it follows

$$M_s = l^{n-1}. \quad (6)$$

If we put Eqs. (5) and (6) into Eq. (4), we get Eq. (2). From Eq. (3), we see that

$$l^n = \prod_k l^{n_k}. \quad (7)$$

Substituting Eq. (7) into Eq. (2) and putting the result in Eq. (1), we obtain finally

$$b_l = \frac{1}{l^2} \sum_{n_k} \prod_k \frac{(l \beta_k)^{n_k}}{n_k!}, \quad (8)$$

$$\sum_k k n_k = l - 1.$$

\* On leave of absence at the California Institute of Technology, Pasadena, California.

<sup>1</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 280, Eq. (13.5).

<sup>2</sup> See reference 1, p. 287, Eq. (13.25).

<sup>3</sup> See reference 1, pp. 455-459.

<sup>4</sup> See reference 1, pp. 285-288.

### Vibrational Fine Structure in the Absorption Spectra of Uranyl and Plutonyl Ions in Aqueous Solution\*

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January 17, 1949

THE absorption spectrum of uranyl ion,  $\text{UO}_2^{++}$ , in aqueous solution at 25°C is unusual in several respects. Uranium in its hexavalent oxidation state has no  $5f$  electrons, so that the weak and narrow absorption bands (characteristic of transitions within the  $f$  shell) which occur in the solution spectra of  $\text{U(III)}$  and  $\text{U(IV)}$  are absent. However, the electronic transition corresponding to the absorption band centering about 4100Å is forbidden as is evident from the low value of the molar absorption coefficient ( $\epsilon=8.5$ ), and is further distinguished by a discrete, though diffuse, regular vibrational structure (Fig. 1, upper part). The band separations of 11 peaks have a mean value of 724  $\text{cm}^{-1}$  for the solution spectrum, which must correspond to the 710- $\text{cm}^{-1}$  interval found in the absorption spectrum of crystalline uranyl salts.<sup>1</sup> In the fluorescence spectrum of uranyl salts<sup>2</sup> the main intervals are 860  $\text{cm}^{-1}$  and are ascribed to the totally symmetric vibration of the O-U-O molecule, for which a Raman shift of 865  $\text{cm}^{-1}$  is observed.<sup>3,4</sup> The 710- $\text{cm}^{-1}$  frequency is for the vibration of the molecule in its electronically excited state corresponding to the 865- $\text{cm}^{-1}$  vibration of the molecule in its ground electronic state. A recent comparison of the uranyl vibrational data has been made by Freymann.<sup>5</sup>

It is known from chemical evidence that the  $\text{Pu(VI)}$  ion is oxygenated and probably has the formula  $\text{PuO}_2^{++}$ . Hence it seemed possible that a band analogous to the uranyl absorption band described above could be found also in the spectrum

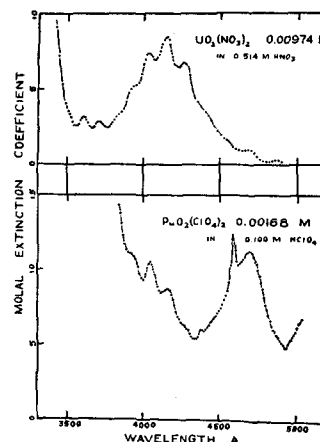


FIG. 1. A section of the absorption spectra of uranyl and plutonyl ions in aqueous solution, showing diffuse vibrational fine structure.

of plutonyl ion in solution. The absorption spectrum of aqueous plutonyl ion is very complex, consisting of many weak and exceptionally narrow bands throughout the visible and adjacent spectral regions. Nevertheless, the expected absorption band with vibrational-like fine structure was found in the 3900-4300Å region for a solution of  $\text{Pu(VI)}$  in 0.1M perchloric acid (Fig. 1, lower part). The same structure is seen somewhat less distinctly in the spectrum of  $\text{Pu(VI)}$  in nitric acid solution,<sup>6</sup> but is obscured in the spectrum of hydrochloric acid solutions of  $\text{Pu(VI)}$ , owing to strong absorption in the same region by  $\text{Pu(VI)}$ -chloride-complexes.

Starting with the 3940Å band of  $\text{PuO}_2^{++}$ , successive frequency intervals of 690, 710, 725  $\text{cm}^{-1}$  are found, giving a mean value of 708  $\text{cm}^{-1}$ , which must correspond to a O-Pu-O vibration in an electronically excited state of plutonyl. A study of the Raman spectrum of plutonyl ion should reveal a frequency shift corresponding to this vibration in the ground state; it should have a value of about 830  $\text{cm}^{-1}$ , analogous to the totally symmetric uranyl vibration frequency.

\* Abstracted from a report to be published in the *Plutonium Project Record, National Nuclear Energy Series*, Atomic Energy Commission Documents MDDC-591 and MDDC-892, July 1946, Oak Ridge, Tennessee.

<sup>1</sup> A. C. S. van Heel, *Commun. Phys. Lab. Univ. Leiden* **187**, 3 (1938).

<sup>2</sup> B. S. Satyanarayana, *J. Mysore Univ.* **4**, 57 (1943).

<sup>3</sup> G. K. T. Conn and C. K. Wu, *Trans. Faraday Soc.* **34**, 1483 (1938).

<sup>4</sup> B. S. Satyanarayana, *Proc. Ind. Acad. Sci.* **A15**, 414 (1942).

<sup>5</sup> M. Freymann, *J. de phys. et rad.* **9**, 158 (1948).

<sup>6</sup> This has been confirmed recently by R. H. Betts and B. G. Harvey, *J. Chem. Phys.* **16**, 1089 (1948).

### Difference in the Recoil Energy of the $\text{Br}^{80}$ Isomers Following Neutron Capture

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January 18, 1949

FOR  $\text{Br}^{80}$  (18 min.) and for  $\text{Br}^{80}$  (4.5 hr.) W. H. Hamill and R. R. Williams<sup>1</sup> have found 0.08 and 0.00 as values for the ratio  $k_6/k_7$  where  $k_6$  and  $k_7$  are defined, according Eqs. (1) and (2):



This result is in agreement with experiments we are going to describe briefly, showing that the complex nucleus emits  $\gamma$ -rays in cascade so that the recoil energy of the  $\text{Br}^{80}$  (18 min.) nucleus is smaller than the recoil energy of the  $\text{Br}^{80}$  (4.5 hr.) nucleus. As a consequence of this, the probability of molecular dissociation is different and also the charge and the nature of the produced ions.

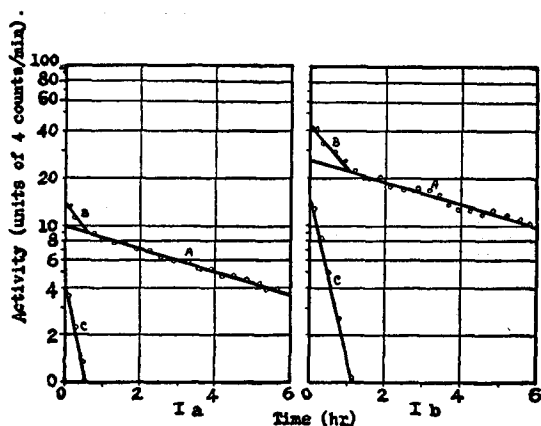


FIG. 1. Isomeric filiation: Ia—Without electric field. Ib—With electric field on the anode. A. Bromine—4.5-hr. activity. B. Bromine—17.4-min. and 4.5-hr. activities. C. Bromine—17.4-min. activity.

TABLE I.

T	Theoretical	$R_0^T$				
		In $\text{CBr}_4$ solid	In $\text{C}_6\text{H}_5\text{Br}$ liquid	Collected on gold plates in $\text{C}_6\text{H}_5\text{Br}$ liquid		
15 min.	33.26	35.8			With field	Without field
30 min.	26.54	26.3			an.	cath.
45 min.	21.72	19.5				
60 min.	18.20			9.5	11.4	7.34
120 min.	10.83	10.1				
360 min.	4.86		4.78	1.7	1.1	1.1
96 hr.	2.92			0.7	0.5	

If we take into account a difference of 86 kev<sup>2</sup> between the ground state (18 min.) and the metastable state (4.5 hr.), we find by a semi-empirical formula<sup>3</sup> that the binding energy of the  $\text{Br}^{79}(n,\gamma)\text{Br}^{80}$  process is 7.24 Mev for the  $\text{Br}^{80}$  (18 min.) and 7.154 Mev for the  $\text{Br}^{80}$  (4.5 hr.). If the full binding energy is emitted as a single  $\gamma$ -ray, the recoil energy would be  $E_r(18 \text{ min.}) = 351 \text{ ev}$  and  $E_r(4.5 \text{ hr.}) = 343 \text{ ev}$ . It is well known that this is highly improbable and that the emission is rather in cascade.<sup>4</sup> If the isomers come from the same capture level, the recoil energy will be the same if the first  $\gamma$ -rays are identically emitted as these determine principally the recoil. Experiments show it is not true.

In a first series of experiments in liquid  $\text{C}_6\text{H}_5\text{Br}$  we confirmed the results obtained by one of us<sup>5</sup> showing separation of the isomers in the electric field during the isomeric transition. After irradiation of 15 hours, the solution is submitted to an electric field (210 volts/cm) for three hours, the electrodes used are gold plates, 2 cm apart. Three hours after irradiation all the  $\text{Br}$  (18 min.) directly formed had gone, and the  $\text{Br}$  (18 min.) collected on the plates is produced by isomeric filiation. The same experiment made without a field shows clearly that the effect is amplified with a field and that the  $\text{Br}^{80}$  (18 min.) is specially collected on the anode. Examples are in Fig. 1.

In a second series of experiments we have studied the primary reaction of the formation of the two isomers of  $\text{Br}^{80}$  by measuring for different periods of irradiation the ratio of the activity of the two isomers:

$$R = \text{activity (18 min.)} / \text{activity (4.5 hr.)}$$

- The total activities produced in  $\text{CBr}_4$  solid and  $\text{C}_6\text{H}_5\text{Br}$  liquid are independent of the recoil effect.
- The activities collected on plates immersed in  $\text{C}_6\text{H}_5\text{Br}$  liquid with an electric field are, however, dependent upon the recoil effect and the charge of the ions.

If we call  $T$  the period of irradiation and  $t$  the time from the end of the irradiation, one finds for the ratio:<sup>6</sup>

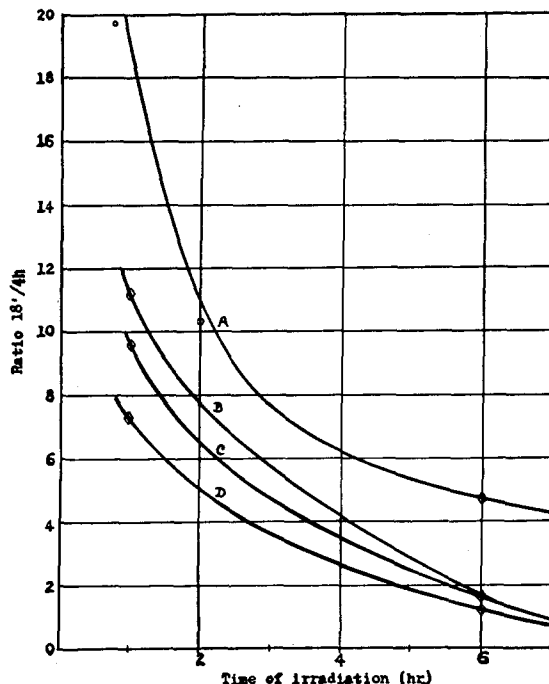


FIG. 2. A. Theoretical curve—experimental point: O with  $\text{CBr}_4$  solid;  $\diamond$  with  $\text{C}_6\text{H}_5\text{Br}$  liquid. B. Collected on gold plates with electric field; cathode. C. Collected on gold plates with electric field; anode. D. Collected on gold plates without electric field.

$$R_t^T = \frac{\sigma_c(18 \text{ min.}) b_T e^{-\lambda_2 t}}{\sigma_c(4.5 \text{ hr.}) (\lambda_1 / \lambda_2 - \lambda_1) \{a_T e^{-\lambda_1 t} - b_T e^{-\lambda_2 t}\}} \quad (3)$$

with  $t=0$ , and  $T$  large Eq. (3) reduce to Eq. (4):

$$R_0^T = \frac{\sigma_c(18 \text{ min.})}{\sigma_c(4.5 \text{ hr.})} \cdot \frac{(1 - e^{-\lambda_2 T})}{(1 - e^{-\lambda_1 T})} = R^\infty \frac{1 - e^{-\lambda_2 T}}{1 - e^{-\lambda_1 T}} \quad (4)$$

where  $\lambda_2$  and  $\lambda_1$  are the radioactive constants for  $\text{Br}^{80}$  (18 min.) and  $\text{Br}^{80}$  (4.5 hr.);  $\sigma_c$  are the capture cross sections and  $R^\infty = 2.92$ .

Table I and Fig. 2 show the results of the experiments.

The results show clearly that the isomers are not collected on the electrodes in the ratio of their formations. The capture cross sections of these isomers are in the ratio 2.92 to 1 at the advantage of the  $\text{Br}^{80}$  (18 min.). Indeed, less (18 min.) are collected on the electrodes. These results show also that it is difficult to get a clear idea of the nature of the ions.

We know that the ratio of the capture cross sections varies with the energy of the incident neutrons<sup>7</sup> and we may find an explanation if we assume that from a single capture level the first and most energetic  $\gamma$ -ray determine the recoil and the cascade leading to one of the isomeric states. For example, we can imagine that the  $\gamma$ -ray of 0.35 of the available energy (the most probable)<sup>4</sup> will give the  $\text{Br}^{80}$  (18 min.) state, while the  $\gamma$ -ray 0.6 of the available energy is three times less probable giving  $\text{Br}^{80}$  (4.5 hr.). The authors know that many other explanations are possible and for this reason experiments must be made where the recoil effect will be studied in gaseous form at low pressure. Working with radioactive bromine (4.5 hr.) we expect to measure the charge of  $\text{Br}^{80}$  (18 min.) at birth from the isomeric transition. These experiments are in progress.

<sup>1</sup> W. H. Hamill and R. R. Williams, J. Chem. Phys. **16**, 1171 (1948).

<sup>2</sup> A. Berthelot, Ann. de physique **19**, 117 (1944).

<sup>3</sup> Clark Goodman, The Science of Nuclear Power (1947), p. 77.

<sup>4</sup> H. A. Bethe, Rev. Mod. Phys. **9**, 233 (1937).

<sup>5</sup> Paul Capron, G. Stokkink, and M. van Meersche, Nature **157**, 806 (1946).

<sup>6</sup> Paul Capron and G. Stokkink, Bull. Acad. Roy. Belg. **32**, 266 (1946).

<sup>7</sup> Paul Capron, Bull. Acad. Roy. Belg. **27**, 524 (1941).