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ANOMALOUSLY LONG RADIATIVE LIFETIMES OF URANYL ION IN SOLUTIONS

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In uranyl solutions, theoretical calculations of natural lifetimes were reported by Rabinowitch *et al*¹ which correspond to an absorption band in the (400–500 nm) region. The value calculated by them ($\tau_{\text{cal}} \sim 1.5 \times 10^{-4}$ sec) was an order of magnitude less than the experimentally observed lifetimes in many cases. They however, mentioned that a correct value could be obtained if, out of the entire absorption curve, the contribution of the electronic absorption corresponding to the F series alone could be evaluated. On the contrary, Dieke *et al*² calculated it to be of the order of 10^{-1} sec. for $\text{CsUO}_2(\text{NO}_3)_3$. This is a much greater value since the fluorescence quantum yield for this uranyl salt is nearly unity. The lifetime of F electronic band calculated by McClynn³ (4.76×10^{-4} sec) is also shorter than the observed values at low temperatures. In our previous work⁴, we calculated the lifetimes, of various uranyl species and found that, in general, for protonated solutions the $\tau_{\text{cal}} > \tau_{\text{obs}}$. This is an expected result as the shortening of the observed lifetimes are due to general non-radiative processes. In the present

paper we report the results of a study with due consideration of fluorescence yield and the lifetimes in deuterated solvents. It is found that the τ_{cal} values are smaller than τ_{obs} values for most of the cases.

The room temperature absorption spectra were recorded with a Beckman DK-2A spectrophotometer. The absorption spectra of uranyl sulphate solution in sulphuric acid were also recorded at 80° K where it froze into a transparent glass, by recording transmitted light of an incandescent source with a monochromator photomultiplier assembly and calculating the extinction coefficient as compared to pure H_2SO_4 frozen glass. The lifetimes and recordings of emission spectra were measured by usual methods⁴.

The natural lifetimes (τ_{cal}) were calculated using the Strickler and Berg⁵ formula.

$$\frac{1}{\tau} = 2.88 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle_{\nu}^{-1} g_i / g_u \int \epsilon(\nu) d \log \nu \text{ sec}^{-1}$$

where n is refractive index, g_i / g_u the multiplicity fac-

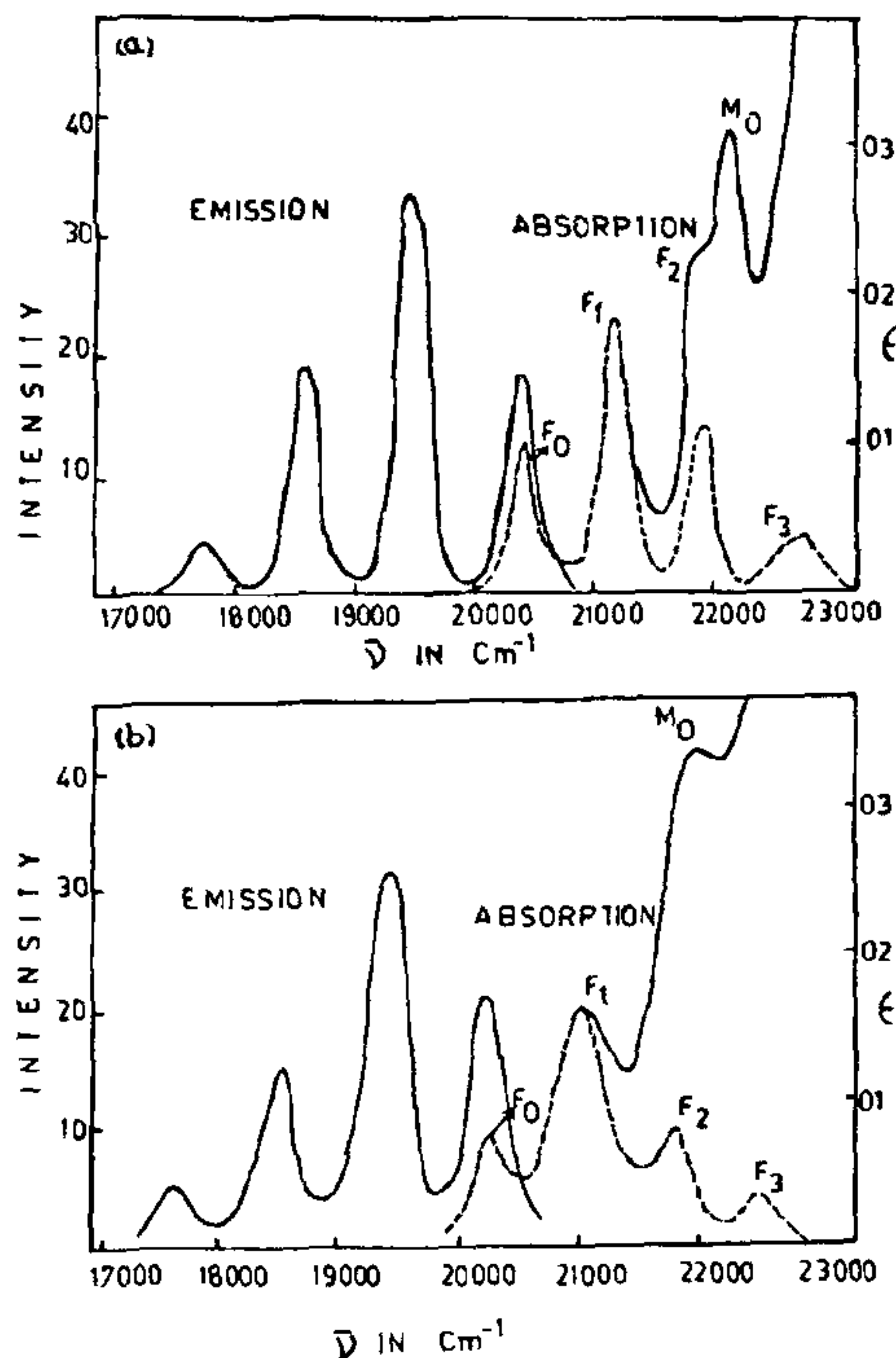


Figure 1. Absorption and emission spectra of the UO_2^{2+} ion in 97% H_2SO_4 solution (a) at 80° K and (b) at 293° K.

tor and $\langle \nu_f^{-3} \rangle_{av}$ is the inverse of the cube of average frequency of fluorescence emission in cm^{-1} . In uranyl salts the emission corresponds to lowest F-electronic series of Dieke and Duncan² and, therefore, in calculating $\int \epsilon(\nu) d \log \nu$ absorption due to F series alone was taken into account. For example in figure 1 (a and b) it is clear that F_0 and F_1 bands are clearly isolated without any overlap of higher members of the series. The other members viz F_2 and F_3 were isolated considering the mirror image symmetry between absorption and emission spectra. It is also clear from the figure that $\int \epsilon(\bar{\nu}) d \log \bar{\nu}$ for $\text{UO}_2\text{SO}_4\text{-H}_2\text{SO}_4$ system is temperature-independent.

The calculated (τ_{cal}) and observed (τ_{obs}) lifetimes are given in table 1. The τ_{obs} values are at 80°K where the lifetimes are almost temperature-independent. From the table it may be observed that in the case of aqueous and acidic solutions of uranyl nitrate, perchlorate and acetate the $\tau_{cal} > \tau_{obs}$ while those for uranyl sulphate show $\tau_{obs} > \tau_{cal}$. The τ_{obs}/τ_{cal} ratio for sulphate solution varies from 1.91 to 2.73 with a maximum for 97% sulphuric acid solution. In order to check the fluorescence quantum yield (ϕ) of this solution we compared its fluorescence yield with 0.1N H_2SO_4 solution of quinine sulphate ($\phi = 0.53$). At room temperature the quantum yield of uranyl sulphate solution was 0.16 which, when multiplied by relative intensity coefficient $I_{80^\circ}/I_{293^\circ \text{K}}$ gives the efficiency nearly unity (0.96). Vavilov and Levshin⁶ have also reported the quantum yield of this solution to be nearly unity. Thus the radiative lifetime ($\tau_{rad} = \tau_{obs}/\phi$) is equal to observed lifetime in this solution and it clearly shows that this case is anomalous. In other uranyl solutions where quantum yield could not be

measured accurately we measured lifetime in deuterated solvents. It is clear that in deuterated solvents the observed lifetimes are close to radiative lifetimes. This is because in these solvents the radiationless transitions are inhibited bringing quantum yields close to unity. A comparison of τ_{obs} in these deuterated solvents with τ_{cal} in the table shows that not only in uranyl sulphate solutions, but also in uranyl nitrate and perchlorate solution the observed lifetimes are 2 to 3 times greater giving an average anomaly factor of nearly three.

An immediate explanation for the anomalously long radiative lifetimes of uranyl solutions cannot be presented. Although there are many other cases in which the radiative lifetimes are anomalously long and some explanations for such anomaly are (a) large interconfigurational changes⁷ (b) inaccurate selection of absorption bands⁸ (c) intramolecular level mixing⁹. (d) Craig and Small effect¹⁰, yet these do not seem to fit in the particular case of uranyl ion. However, as a consequence of our experimental results the following reasons can also be considered. As the anomaly can be averaged by a factor of three, there is likelihood of the F electronic state being the triplet. But there is no definitive argument to suggest this. Secondly, the Strickler and Berg formula may not be applicable in the case of molecular transitions though it is used most commonly. Any definite explanation for the anomaly requires further study.

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TABLE I

Table for natural lifetimes τ_{cal} and observed life time for uranyl ion in various protonated $\tau_{obs}(H)$ and deuterated $\tau_{obs}(D)$ solutions at 80°K .

Salt	Solvent	τ_{cal} ($\mu \text{ sec}$)	$\tau_{obs}(H)$ ($\mu \text{ sec}$)	$\tau_{obs}(D)$ ($\mu \text{ sec}$)	$\frac{\tau_{obs}(H)}{\tau_{cal}}$	$\frac{\tau_{obs}(D)}{\tau_{cal}}$
$\text{UO}_2(\text{NO}_3)_2$	H_2O	700	250	1600	0.40	2.23
UO_2SO_4	H_2O	222	425	700	1.91	3.18
UO_2SO_4	$\text{H}_2\text{SO}_4(25\%)$	198	450	580	2.27	2.92
UO_2SO_4	$\text{H}_2\text{SO}_4(50\%)$	214	510	630	2.38	2.94
UO_2SO_4	$\text{H}_2\text{SO}_4(75\%)$	279	630	780	2.43	2.80
UO_2SO_4	$\text{H}_2\text{SO}_4(97\%)$	340	930	1120	2.73	3.30
$\text{UO}_2(\text{ClO}_4)_2$	H_2O	620	300	1600	0.48	2.58
$\text{UO}_2(\text{ClO}_4)_2$	HClO_4	650	300	—	0.46	—
$\text{UO}_2(\text{CH}_3\text{COO})_2$	H_2O	491	340	560	0.69	1.14
$\text{UO}_2(\text{CH}_3\text{COO})_2$	CH_3COOH	635	300	—	0.47	—

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ANALOGUES OF HOUSE FLY ATTRACTANT, MUSCALURE

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CARLSON *et al*¹ isolated muscalure from cuticular lipids of mature female housefly, *Musca domestica*. They identified muscalure as (Z)-9-tricosene and confirmed its structure by synthesis and further showed by bioassay that the synthetic product is a potent attractant for male house flies. Since then several reports²⁻⁶ have appeared describing synthesis of muscalure and its homologues.

We report here bioassay of seven molecular analogues of muscalure prepared⁷ by Kolbe electro-organic synthesis. All analogues are long chain carbon compounds containing either 23 or 24 carbon atoms with either oxirane function or *cis*-disubstituted double bond at C-9 atom and presence or absence of hydroxyl at C-7.

Bioassay for pheromone activity was essentially carried out as described by Carlson *et al*¹. Each experiment is for 15 min, and an average of three such experiments is taken to assess the activity. The number of flies attracted to muscalure, minus the number of flies attracted to air alone is taken as 100% activity. Activities of other compounds are expressed as percent of activity of muscalure (table 1).

TABLE I

Pheromone activity of muscalure analogues.

Compounds	Pheromone activity†
Muscalure (Z)-9-tricosene	++
(Z)-9-tetracosene	+
9-epoxy-tricosane	0
9-epoxy tetracosane	0
7-hydroxy-(Z)-9-tricosene	+
7-hydroxy-(Z)-9-tetracosene	++
7-hydroxy-9-epoxy-tricosane	0
7-hydroxy-9-epoxy-tetracosane	0

- † Pheromone activity tested on housefly adults
++ indicates significant pheromone activity like muscalure about (80-100%)
+ indicates moderate pheromones activity (about 40%)
0 indicates no pheromone activity (less than 10%)

The results indicated that the presence of *cis*-double bond at C-9 was essential for pheromonal activity. The presence of hydroxyl group at C-7 atom did not affect the activity adversely; in fact activity was increased in the C-24 compound. All other compounds where the double bond was epoxidised, the activity was lost.

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