Title
OPTICAL PROPERTIES OF TETRAVALENT URANIUM IN THE SOLID STATE

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Optical spectra of f^n ions are characterized by intra-configuration transitions which are relatively sharp. For trivalent lanthanide ions diluted in non-interacting host crystals (i.e. $Pr^{3+}/LaCl_3$) linewidths obtained by conventional optical spectroscopy techniques are the order of 1 cm^{-1} [1,2]. Tetravalent U^{4+} ions usually have linewidths on the order of 1-10 cm^{-1} [3]. Some U^{4+} ions diluted in Th tetrahalide crystals have peculiar line shapes due to an incommensurate structure of the host crystal. These anomalous results have been thoroughly studied [4].

For f^n ions in sites with inversion symmetry, the zero phonon electronic transition may not be observed. Instead, a zero phonon electronic transition plus one or more vibrational transitions are found. By assigning the vibrational transitions the zero phonon electronic transition may be inferred [5-8].

Once the optical spectra have been obtained, the data are fit to the parameters of a phenomenological Hamiltonian from which a calculated spectrum is obtained. The goodness of fit is determined by the value of σ (in cm^{-1}), the rms deviation, defined as

$$\sigma = \sum_i \left[\frac{(E_{i(exp)} - E_{i(calc)})^2}{n - p}\right]^{1/2}$$

where $E_{i(exp)}-E_{i(calc)}$ are the ith experimental and calculated levels, respectively, n is the number of assigned levels, and p is the number of free parameters [9]. For the trivalent lanthanide ions in $LaCl_3$, σ ~8-20 cm^{-1}, and for the trivalent actinide ions in $LaCl_3$, σ ~20 cm^{-1}.

The magnitude of the crystal field depends strongly on the type of host crystal and the distances of the nearest neighbor ions to the f^n ion. A qualitative measure of the magnitude of the crystal field is provided by the parameter first defined by Auzel [10]:

$$\frac{N_v}{\sqrt{4\pi}} = \left[\sum_k \frac{(B_q^k)^2}{(2k+1)}\right]^{1/2} .$$

The Table lists U^{4+} in various host crystals plus, for comparison purposes, Pr^{3+} or Nd^{3+} in various crystals and the free ion U^{4+} [11-22].

There are a number of noteworthy trends in this Table. First of all, the rms deviation σ for the U^{4+} compounds is much worse on the average than found for the Pr^{3+} or Nd^{3+} examples. Only in the best case does the σ for a U^{4+} compound approach that of the lanthanide ion. The U^{4+} organometallic compounds fit poorly. Most of the data available for these compounds are for the low-lying levels and the free ion parameters are not well determined. The centrosymmetric complexes UCl_6^{2-} and UBr_6^{2-} have been the subject of intensive studies, and the data appear extremely reliable. Nevertheless, they are among the worst-fitting cases. Similarly, the data for $U^{4+}/ZrSiO_4$ is quite extensive, yet the fit is poor.

Finally, there appears to be a correlation between a poor fit and a large value of σ. In most cases the fit is worse when the value of the parameter $N_v/\sqrt{4\pi}$ is large indicating a very strong crystal field.

It is difficult to know how to proceed. Some directions to be tried or already underway are:

- Reexamination of the parametric theory to see if other interactions can be included [23,24];
- Ab initio calculations of U^{4+} molecular or cluster systems such as $U(BH_4)_4$ or UCl_6^{2-} [25];
- Optical studies of higher atomic number tetravalent ions to determine the sytematics of the series [26,27];
- The use of polarized neutrons to study directly bonding or covalency effects [28].

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Table. Summary of Some U^{4+} Optical Data Plus Some Other Systems

System	No. Levels Assigned	σ (cm^{-1})	$N_v/\sqrt{4\pi}$ (cm^{-1})	Ref.
$U^{4+}/ThBr_4$	26	36	1544	11
$U^{4+}/ThCl_4$	25	46	1560	12
UCl_4	26	60	1602	13
$U^{4+}/ThSiO_4$	25	71	1617	14
$U^{4+}/ZrSiO_4$	30	112	3113	15
$U(BD_4)_4/Hf(BD_4)_4$	19	~52	4346	16
$[Cp_3U(NCS)_2]^-$	18	>250	2923	17
$[Cp_3U(NCBH_3)_2]^-$	18	>250	2943	17
UBr_6^{2-}	26	>225	3167	18
UCl_6^{2-}	21	>150	3471	18
Cp_3UCl	27	125	3143	19
$PrCl_6^{2-}$	27	14.8	980	20
$Nd^{3+}/LaCl_3$	10	8.1	300	21
U^{4+} (free ion)	13	9.8	—	22

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