SPECTROSCOPIC PROPERTIES OF Bk$^{3+}$ AND Cf$^{3+}$

by

W. T. Carnall (with S. Fried)

For Presentation At:

Symposium Commemorating the 25th Anniversary of the Discovery of Elements 97 and 98, Lawrence Radiation Laboratory, Berkeley, California, January 20, 1975
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It was Burris Cunningham and co-workers who at an American Chemical Society meeting in 1958 first pointed out the special significance of Bk$^{3+}$ and Cf$^{3+}$ to actinide spectroscopy. The limits they could place on the intensities of absorption bands in the solution spectra of Bk$^{3+}$ and Cf$^{3+}$ were consistent with the return to a more lanthanide-like intensity pattern in the second half of the actinide series. This made it clear that it would be important in the future to study in detail the spectroscopy of these two elements. The prospect of the return to a more lanthanide-like character becoming clearly established in Bk$^{3+}$ and Cf$^{3+}$ suggested that an understanding of their energy-level structures could provide the key to predicting the spectroscopic properties of all of the heavier trivalent actinides. The very short half-lives associated with the heaviest members of the series essentially precludes any extensive experimental spectroscopic investigation of them.

In 1962-63 the first spectroscopic observations in the solid state were reported. Using 1 µgm quantities of the elements, the groups at Berkeley and Livermore succeeded in observing a number
of lines in both the absorption and fluorescence spectra of \( \text{Bk}^{3+}:\text{LaCl}_3 \) and \( \text{Cf}^{3+}:\text{LaCl}_3 \). Three years later in 1966, Green and Cunningham\(^4\) were able to grow a small single crystal of \( ^{249}\text{CfCl}_3 \), and extend the region of observation into the near infrared.

As the heavy element production program of the AEC began to yield milligram quantities of Bk and Cf, we at Argonne undertook the first extensive low temperature spectroscopic studies of the pure halides, \( \text{BkCl}_3 \)\(^5\) and \( \text{CfCl}_3 \).\(^6\) Solid state spectroscopy continues to be a very productive and exciting area for investigation. The definitive single crystal work with \( \text{Bk}^{3+}:\text{LaCl}_3 \) and \( \text{Cf}^{3+}:\text{LaCl}_3 \) is only now in the active planning stage. The experiments will be conducted in a joint effort involving groups at LBL and ANL. Such cooperative efforts have frequently been undertaken. In the context of the present subject, our initial joint experiments grew out of a set of unique circumstances that led, in 1965-66, to the first measurements of the solution absorption spectrum of \( \text{Cf}^{3+} \) using macroscopic quantities of the element.

**First Solution Spectra with Macro Quantities of Bk and Cf**

We at ANL were sending a spectrophotometer back to a factory in California for optical modifications in the fall of 1965. The group at LBL had separated 167 \( \mu \text{gm} \) of Cf, mainly \( ^{252}\text{Cf} \), and was quite amenable to a joint spectroscopic experiment if some means of making the measurement could be found. With the indicated
quantity of $^{252}\text{Cf}$, all operations were of course restricted to a cave. Consequently, the "Hot Lab" group\textsuperscript{7} at ANL developed a set of remote controls for our spectrophotometer, we designed some micro spectrophotometer cells that could be loaded and handled with manipulators, and we arranged to ship our spectrophotometer to the factory via Berkeley. It was duly placed inside a cave and spectra were recorded in September 1965.

By the end of the year, more $^{252}\text{Cf}$ had been separated and purified, so the now optically modified instrument was shipped back to ANL via Berkeley. Figure 1 is an example of spectra we recorded using 592 \(\mu\text{gm}\) of $\text{Cf}^{3+}$ in a 2 cm x 2 mm diameter capillary cell of approximately 250 \(\mu\text{l}\) volume. The coincidence in date with this symposium is apparent. The spectrum was recorded January 20, 1966 (pm).

The type of capillary cell used is shown in Figure 2. There are of course a number of problems associated with such an experiment not the least of which is the decomposition of the solvent by the intense radiation. In deference to the location, we noted in our published results\textsuperscript{8} that the samples had the bubbling characteristics of fine California champagne. The increasing background shown at $>9500 \text{Å}$ in Figure 1 was caused by bubbles accumulating and finally blocking light from passing through the cell. The remedy was to carefully remove the cell from the spectrophotometer, shake it to dislodge the bubbles, replace it in the spectrophotometer and quickly run another segment of the spectrum. With a good portion of the world's supply of Cf involved at the time you can be certain the operation began with extreme caution. I wish we had recorded the progress of the experiments on film because it would certainly have
been hilarious to compare the initial caution, with the increasing sense of urgency as the experiments progressed. With confidence gained the cell was removed from the spectrophotometer, then within one minute vigorously shaken, rapidly replaced, and a new scan begun. One can judge the effort involved by the fact that individual scans never exceeded 2 min before the cell was again blocked. The operation would have been impossible without the patience and full cooperation of all involved, particularly the cave crew and the radiation monitoring group. Figure 3 shows the excellent agreement between the results reported in our 1966 publication and data taken more recently at ANL using milligram quantities of $^{249}\text{Cf}$. 

The cooperative effort with Cf was so successful that as multi-microgram quantities of Bk became available we resolved to again perform a joint experiment. This time it took place at Livermore in the summer of 1966 using the same microcell techniques. Of course since $^{249}\text{Bk}$ was involved, no elaborate shielding was necessary. With 45 $\mu$gm of $^{249}\text{Bk}$, enhancing the weaker bands using elaborate time-averaging techniques followed by computer processing, we obtained the first solution spectrum of $\text{Bk}^{3+}$, Figure 4. These results were also in good agreement with spectra recorded later at ANL using several milligrams of Bk.

We were able to oxidize $\text{Bk}^{3+}$ to $\text{Bk}^{4+}$ in that first experiment, but all of the bands were superimposed on a strong ultraviolet absorption. Later at ANL we repeated this work with larger quantities of Bk and showed that even in the visible region the $\text{Bk}^{4+}$ band occurred at the same energy as a prominent band in $\text{Bk}^{3+}$, Figure 5. In dilute $\text{H}_2\text{SO}_4$ we could readily oxidize Bk to $\text{Bk}^{4+}$,
then reduce it to Bk\(^{3+}\) with SO\(_2\) without transferring the sample.

This clearly delineated the regions of absorption as contrasted to the rather significant background.\(^{10}\)

Theoretical Treatment of the Energy Level Structures

For some of us, interest in actinide spectroscopy has centered around the development of a theoretical model which can be used as a basis for computing the entire energy level scheme for each actinide ion. Relationships between ionic structure and absorption spectra are also worthy of exploration. There is a wealth of information contained in the solution absorption spectra itself, but to exploit this, one needs a firm base upon which to build, and this requires crystalline samples where the spectroscopic states can be characterized using such experimental techniques as polarization and Zeeman effect.

Theoretical interpretation is a developing process. Our first work was of course with the light actinides. Since the spectra we observe in the 3+ actinides are for the most part characteristic of transitions within the 5f\(^N\)-configuration, we can expect that the parameters of any model which describes these interactions should vary rather uniformly across the series. Paul Fields, Brian Wybourne and I made our first predictions of the energy level structure of Bk\(^{3+}\) and Cf\(^{3+}\) in 1964,\(^{11}\) so it has been of particular interest to us to determine how and why these predictions have had to be modified as experimental data became available.
Before briefly outlining the theory, it is useful to emphasize what it is that we observe and what we are attempting to calculate. The region of the absorption spectrum of Bk$^{3+}$ included in Figure 6 shows the resolution of several LSJ-states into crystal-field components at the temperature of liquid helium. Experimentally, the spectrum was obtained in transmission through a thin film of BkCl$_3$. We assume that the crystal-field splitting of any J-level can be treated as a perturbation of the free-ion structure. Thus the theoretical model is primarily concerned with accurately reproducing the free-ion structure which in this case is experimentally defined by the centers of gravity of the components identified with each J-state. Since the transitions are all within the 5f$^N$-configuration, which is well shielded from the environment, we further argue that to a good approximation the energies of the free-ion states in BkCl$_3$ or CfCl$_3$ are not much different from those that would be observed in a low pressure gas of the ions. In fact there should be a strong correlation between the structure of the Cf$^{3+}$($5f^9$) configuration and that of the configuration 5f$^96s^2$ in BkI.

The principal interactions included in the free-ion Hamiltonian are outlined in Figure 7. We can summarize by pointing out that the energy level scheme calculated based solely on the interactions that are primarily responsible for the structure of the f$^N$-configuration, $H_E$ and $H_{SO}$, is in poor agreement with the experimental results. This is true regardless of whether one uses Hartree-Fock methods to calculate $F_k$ and $\zeta_f$ or a procedure that treats these terms as parameters to be defined by a least squares fit to the experimental data.
The perturbing effects of configuration interaction must be explicitly included in the model in order to obtain a good correlation with experiment. This is done by the inclusion of effective operators that represent important classes of configuration interaction such as those indicated in Figure 7.\(^{12}\)

A model that included the effects of the two-body interactions, \(H_{\text{CI}(2)}\), proved useful in correlating the experimental results obtained for the light actinides. Extrapolated to \(\text{Cf}^{3+}\), it predicted that the observed free-ion structure would be consistent with that indicated in Figure 8 for values of \(F_2\) in the range 260-280 cm\(^{-1}\). Notice that a number of states rather isolated in energy were to be expected. Results such as those shown in Figure 9 for the lowest energy \(J = 11/2\) and \(9/2\) states in \(\text{CfCl}_3\) appeared to correlate quite well with the extrapolated energy scheme. A small adjustment in the parameters of the model based on the actual observed free-ion energies in \(\text{BkCl}_3\) and \(\text{CfCl}_3\) confirmed a developing regular behavior in the heavy actinides which, although the data was incomplete, appeared to account for the principal features observed in the absorption spectrum of the next heavier actinide, \(\text{Es}^{3+}\).\(^{13}\)

At this point there was still considerable room for improvement in the correlation between calculated and observed free-ion levels. One means of accomplishing this was to expand the theoretical model. H. M. Crosswhite, Hannah Crosswhite and I have recently been attempting to do this, and it has become increasingly apparent that with the inclusion of the three-body effective operators in Judd's formulation, together with several smaller magnetic and electrostatic interactions,\(^{12}\) we now have a model that is sufficiently detailed for present purposes. As we have been able to determine the
parameters of the model, it has been found that they assume values characteristic for the whole actinide or lanthanide series.

Crystal Field Interactions

Until the experimental work on single crystals of the actinides is much more complete, we can use the theory to predict, but we can also note the correlations that are apparent from data that have been reported. Figure 10 shows the splitting of the ground state in isoelectronic lanthanides and actinides for the ions doped into single crystal LaCl₃. The identical ordering of the levels in terms of the crystal-field quantum numbers (μ) is obvious as far as experiment has gone. All the heavier actinide trichlorides through EsCl₃ exhibit the same UCl₃-type structure that is characteristic of LaCl₃. It is now apparent that the correlation in ground state level ordering carries over into the heavier members of both series.

In our investigation of the low temperature spectrum of BkCl₃, it became obvious that the absence of transitions to excited J = 0 and J = 1 states whose approximate energies could be established from the calculation constituted good evidence for a μ = 0 ground level consistent with the case of Tb³⁺:LaCl₃. Similarly in CfCl₃ we could infer the existence of a μ = 3/2 ground state consistent with that of Dy³⁺:LaCl₃. All of the components of several excited J-states appeared to have been observed at 4°K. This would not be expected if values of μ = 1/2 or 5/2 were associated with an isolated ground state in CfCl₃.
Working with $^{3+}\text{U}:\text{LaCl}_3$ we recently carried out the first complete crystal-field calculation for an actinide ion, simultaneously diagonalizing the matrices of the expanded free-ion model with the crystal-field. The results confirm that the crystal-field in compounds of the $3^+$ actinides can be treated as a perturbation, over a wide range of energies as long as the centers of gravity of the levels are accurately reproduced. With the cooperation of N. Edelstein at LBL, this type of calculation is being expanded to heavier actinides. In preliminary calculations, we find excellent correlation with experiment for $^{3+}\text{Np}:\text{LaCl}_3$ and $^{3+}\text{Pu}:\text{LaCl}_3$. Within the last few weeks we have used the crystal-field parameters obtained in a preliminary fit of data for $^{3+}\text{Pu}:\text{LaCl}_3$ together with an expanded free-ion parameterization for $\text{CfCl}_3$ to perform a preliminary crystal-field calculation for $\text{CfCl}_3$. Some of the features of the $\text{Cf}^{3+}$ spectrum that were difficult to understand appear to have their origin in low-lying double levels in the ground state. At this point we can predict that $^{3+}\text{Cf}:\text{LaCl}_3$ should have extremely interesting magnetic properties with two crystal field components, $\mu = 3/2$ and $5/2$ lying very near the zero of energy. We look forward with considerable anticipation to the projected cooperative studies of $^{3+}\text{Bk}:\text{LaCl}_3$ and $^{3+}\text{Cf}:\text{LaCl}_3$.

**Crystal Spectra-structure Correlations**

As our experimental studies of Bk and Cf halides have expanded, new insights into spectra-crystal structure relationships have become apparent. For example, the spectra of $\text{CfCl}_3$, $\text{CfBr}_3$, and
CfI$_3$ at ~4°K are shown in Figure 11. Within the indicated energy range we expect transitions to excited $J = 11/2$ and $9/2$ states. The appearance of bands in CfBr$_3$ near 7000 cm$^{-1}$ is significant. It suggests that in all probability there are also higher energy bands in CfCl$_3$ than we have observed. The relative intensity of the ~6500 cm$^{-1}$ band in CfBr$_3$, and both the energy and intensity of the only group observed for CfI$_3$ in this range provide the basis for additional interpretation of the spectra.

Some of the crystal structure types characteristic of certain actinide and lanthanide halides are summarized in Figure 12. That we would see different splittings of the same $J$-levels (Figure 11) is expected since three different structure types are involved. However the intensity relationships are of particular importance.

Intensity Relationships

The intensity associated with certain transitions in the $3^+$ actinides and lanthanides is strongly dependent upon the host. The term hypersensitivity has been used in connection with this phenomena. What is meant may be illustrated by comparing the room temperature spectra of the same ion in two different hosts; one where the enhanced intensity is observed and the other where the "usual" intensity pattern prevails. Throughout the spectrum, all the band intensities will be comparable on a molar absorptivity basis except for one or two transitions where in the host inducing hypersensitivity the corresponding band may show a 5-10 fold increased intensity. The transitions that may exhibit hypersensitivity have been identified in calculations based on the Judd-Ofelt intensity theory.
For present purposes, suffice to say that the transition to the first $J = 11/2$ state in $\text{Cf}^{3+}$ is predicted to exhibit hypersensitivity in an appropriate host whereas that to the first $J = 9/2$ state will not. Such pronounced intensity as is observed in $\text{CfBr}_3$ near 6550 cm$^{-1}$ suggests that the crystal structure involved constitutes a hypersensitive host. The only band observed in this range in $\text{CfI}_3$ is also consistent with a hypersensitive host. There is therefore an indication that the $J = 11/2$ lies generally lower than that of $J = 9/2$.

We first noticed that the $\text{BiI}_3$-structure can induce hypersensitive transitions when we were investigating the spectra of the $\text{Am}^{3+}$ halides. At that time it was still thought that the orthorhombic $\text{PuBr}_3$-type structure extended through $\text{AmI}_3$. Comparison of intensity patterns in $\text{PuI}_3$ and $\text{AmI}_3$ suggested this was not the case. As we were completing our spectral studies, Asprey, Keenan, and Kruse published the results of an investigation of the x-ray powder patterns of the Am and Cm halides. They pointed out that indeed there is a structural change at $\text{AmI}_3$ with the stabilization of the 6-coordinate hexagonal structure, in contrast to earlier reports. The spectroscopic results with $\text{CfI}_3$ are consistent with the same structure. The spectroscopic results on $\text{BkBr}_3$ show no evidence of hypersensitive transitions, nor do any of the other lighter actinide tribromides. A change is obvious in $\text{CfBr}_3$. Burns and Peterson have ascribed the monoclinic $\text{AlCl}_3$ structure to $\text{CfBr}_3$ noting that dimorphism may be involved. We have now shown experimentally that hypersensitive transitions are also observed in the heavy lanthanide trichlorides.
Calculation of Transition Probabilities

The Judd-Ofelt theory has already been mentioned in connection with the prediction of hypersensitive transitions. It was derived as a basis for quantitative calculation of the intensities of bands observed in f-electron spectra. The electric dipole oscillator strength of an absorption band can be expressed as shown in Figure 13. Judd showed that the parameters of the theory could be evaluated from the solution spectra of lanthanide ions. We at ANL confirmed the validity of the theory, performing the required calculations and experimental work for the whole lanthanide series. Early attempts to extend the theory to the actinides were not very successful because we had a poor understanding of the energy level schemes. With considerable progress made in energy level correlations, we have returned to the intensity studies. The results for Cf$^{3+}$(aquo) shown in Figure 14 confirm the validity of the method. However such results also indicate an important area for development in actinide spectroscopy.

We are in the process of extending such calculations to solid compounds of the actinides. The parameters, $T_\lambda$, are evaluated from absorption measurements, but they are constants of the system. Thus they can be used to predict the most intense transitions in fluorescence. Indeed a large field of laser technology is being developed around the Judd-Ofelt theory as an important part of a general method for predicting and evaluating the efficiency of laser transitions in different hosts. Important contributions to this area have been made
in lanthanide systems by groups at LLL, particularly W. F. Krupke, M. Weber and their co-workers. The work with actinides is just beginning.

Other Valence States

In closing, it is appropriate to point out that we are only beginning to study and interpret the spectra of valence states of actinide ions other than the 3+. The spectrum of Bk$^{4+}$(aquo) has already been noted. From Figure 15, taken from Brewer's work, it can be predicted that intense broad bands characteristic of f → d transitions should arise in the spectrum of Cf$^{2+}$ near 20,000 cm$^{-1}$. Our experimental study of a sample of CfBr$_3$ after treatment with H$_2$ at ~600°C, Figure 16, reveals the presence of strong bands at the predicted energy. This suggests that Cf$^{2+}$ will be a particularly good system in which to study the weaker f → f transitions, since a wide spectral range is available.

In spectroscopic terms, this paper has dealt with the 3rd, 4th, and 5th spectra of some of the heavy actinides. The prospects for future interesting and rewarding investigations are substantial. One of the results of our detailed study of trivalent ion energy level schemes should be new insights into the interpretation of the much more complex atomic spectra, a subject which is to be discussed by my colleague John Conway in the next paper.
REFERENCES


7. H. Youngquist (supervisor), W. Mohr, J. Van Loon, J. Hoh, and G. Mack were among the members of this group at ANL.


BERKELEY:
J.G. CONWAY
S. FRIED
R.M. LATIMER
R.Mc LAUGHLIN

20 JANUARY 1966 (p.m.)
(Cf$^{3+}$ in 250 λ 1M DCIO$_4$+5-10%CD$_3$OD
592μg. Cf
2 cm x 2 mm diam. cap. cell

LIVERMORE:
R.G. GUTMACHER

ARGONNE:
W.T. CARNALL
P.R. FIELDS

WAVELENGTH (Å)
Figure 4

Bk$^{3+}$ (1 M DCI) (1966)

Bk$^{3+}$ (0.1 M HClO$_4$ - DCIO$_4$) (1974)
ABSORPTION SPECTRA
of Bk$^{3+}$ and Bk$^{4+}$ in 0.4 M $D_2$SO$_4$
FIGURE 6
The total energy of a system consisting of a point nucleus surrounded by N electrons can be represented by the Hamiltonian:

\[ H = H_0 + H_E + H_{SO} + H_{CI} + H_{CF} \]

- **H₀** (Involves the kinetic energy of the electrons and their interaction with the nucleus)
- **Hₑ** (Electrostatic term) \[ E_e = \sum_{k=0}^{6} f^k \]
- **Hₘₖ** (Spin-orbit interaction) \[ E_{SO} = A_{SO} \zeta_f \]
- **Hₘₖ** (Configuration interaction)
  - \( H_{CI}(2) = \alpha L(L+1) + \beta G_G + \gamma G_R \)
  - **Hₘₖ** (Three-particle operators)
  - **Hₘₖ** (Spin-other orbit interaction)
  - **Hₘₖ** (Spin-spin interaction)
  - **Hₘₖ** (Electrostatically correlated spin-orbit interaction)

**Hₚ** (Crystal-field interaction)
GROUND STATE STRUCTURE
for Trivalent Lanthanides and Actinides
in Hexagonal \((UCI_3\) Type) Lattices

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<th>(f^5(6H_{5/2}))</th>
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| \(Eu^{3+}\) | \(3\mu\) E       | \(2\mu\) E    | \(2\mu\) E         | \(2\mu\) E    | \(2\mu\) E       |
| \(Am^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |
| \(Gd^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |
| \(Cm^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |

| \(Er^{3+}\) | \(2\mu\) E       | \(2\mu\) E    | \(2\mu\) E         | \(2\mu\) E    | \(2\mu\) E       |
| \(Ho^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |
| \(Es^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |
| \(Dy^{3+}\) | \(2\mu\) E       | \(2\mu\) E    | \(2\mu\) E         | \(2\mu\) E    | \(2\mu\) E       |
| \(Cr^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |
| \(Tb^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |
| \(Bk^{3+}\) | \(\mu\) E        | \(\mu\) E     | \(\mu\) E          | \(\mu\) E     | \(\mu\) E        |

\(E\) is energy in \(cm^{-1}\)

*FIGURE 10*
FIGURE 11
BAND INTENSITY CALCULATIONS

- Experimental

\[ P = 4.3 \times 10^{-9} \int \varepsilon_i(\sigma)d\sigma \]

where \( \varepsilon_i(\sigma) \) is the molar absorptivity at a given energy \( \sigma(\text{cm}^{-1}) \)

- Theoretical

\[ P^D = 4.0 \times 10^{-11} \sigma(\psi J\|L + 2S\|\psi'J')^2 \eta/2J + 1 \]

where the non-zero matrix elements will be those diagonal in \( S \) and \( L \), and \( \eta \) is the refractive index of the medium.

Judd-Ofelt Theory

\[ P_{E.D.} = \sum_{\lambda \text{ even}} T_\lambda \sigma(f^N\psi J\|U^{(\lambda)}\|f^N\psi'J')^2 \]

\[ \lambda = 2, 4, 6 \]

where \( T_\lambda \) are the parameters of the model, and the reduced matrix elements of \( U^{(\lambda)} \) are computed from the intermediate coupling eigenvectors.
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\[
\frac{T_2 \times 10^9}{0.306} \quad \frac{T_4 \times 10^9}{1.005} \quad \frac{T_6 \times 10^9}{1.718}
\]

**FIGURE 14**
Energy differences between the lowest-lying states in the $5f^N$ and $5f^{N-1}6d$ configurations in the $+2$ through the $+4$ spectra of the actinides where $N = Z - 88$ for $\text{An}^{2+}$, $N = Z - 89$ for $\text{An}^{3+}$, and $N = Z - 90$ for $\text{An}^{4+}$. 

**Figure 15**

*Graph showing energy differences for various actinides.*
I.6F

\[
\text{CfBr}_3 - \text{CfBr}_2
\]

A \( \text{CfBr}_3 + \text{CfBr}_2 \) (He)
B \( \text{CfBr}_3 + \text{CfBr}_2 \) (LN)
C \( \text{CfBr}_3 \) (pure) (He)

\begin{align*}
\text{WAVELENGTH} & \quad 30000 \quad 25000 \quad 22500 \quad 20000 \quad 17500 \quad 15000 \\
\text{cm}^{-1} & \quad 0.32 \quad 0.36 \quad 0.40 \quad 0.44 \quad 0.48 \quad 0.52 \quad 0.56 \quad 0.60 \quad 0.64 \quad 0.68 \\
\text{ABSORPTIVITY UNITS} & \quad 1.6 \quad 1.4 \quad 1.2 \quad 1.0 \quad 0.8 \quad 0.6 \quad 0.4 \quad 0.2 \quad 0.0
\end{align*}