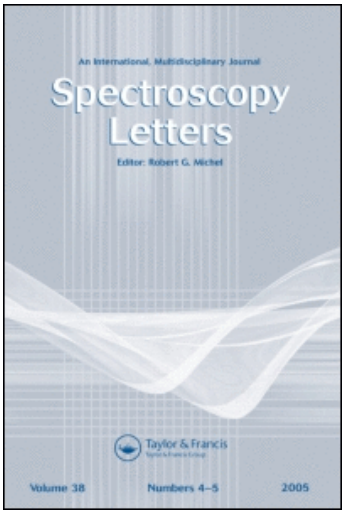

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PHOTOACOUSTIC AND ABSORPTION SPECTRA OF UF_4

KEY WORDS: Photoacoustic Spectroscopy, UF_4

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INTRODUCTION

The visible and near IR spectrum of the U^{4+} ion has been studied by several authors, including aqueous solution studies[1] and work on UF_4[2,3], UCl_4[4], and U^{4+} in CaF_2[5]. The last experiment resulted in a spectrum which was sharper than that obtained for pure UF_4, and the spectra features were assigned according to the prescription of Spedding.[6] While good agreement between the calculated and experimental energies was obtained, the matter of U^{4+} site symmetry in CaF_2 has not been resolved. The actual symmetry of U^{4+} in UF_4 is an eight-cordinate, distorted square antiprism with U-F bond distances ranging from 2.249 Å to 2.318 Å (cf ref. 7,8). Such low U^{4+} site symmetry makes a group theoretical analysis of electronic states from the f^2 ion of little aid in the assignment of the Russel-Sanders atomic states and their respective J term microstates. This

low site symmetry, and the resulting J term splitting, may in part cause the wide peak widths observed in UF_4 (and UO_2).

We have measured the photoacoustic spectrum of UF_4, extending the previously reported spectrum into the range from 800 nm to 2600 nm. Spectra at cryogenic temperatures were recorded for UF_4 in KBr pellets to assess the role of phonons in the broad spectral features of UF_4. A room temperature PAS spectrum of UO_2 also has been obtained for comparison. These data have been compared with those of Conway[5] and Hecht and Gruber[4], and we have found qualitative agreement between the energies of these prior studies and those obtained in this study. We interpret the broad spectral peaks we have observed in UF_4 compared to the narrow features seen in dilution studies as being derived from lower site symmetry of the U^{4+} species and/or uranium-uranium interactions. Shifts in peak maxima are attributed to differences in uranium-anion interaction.

EXPERIMENTAL

Three UF_4 samples were prepared 1) UF_4 powder (~325 mesh) was used neat, 2) UF_4 vapor was deposited on a sapphire disk under vacuum using UF_4 powder, heated in a graphite crucible to ~600°C, and 3) and a mixture of approximately 1:20 UF_4 powder in KBr was pressed under vacuum resulting in a light green transparent pellet. A neat, dark brown UO_2 powder also was examined.

The photoacoustic spectra of the samples were obtained with an EG&G PARC Model 6001 spectrometer.[9] The light source was a electronically modulated 1kW xenon air lamp compensated by a pyroelectric reference detector. These and all other components of the spectrometer, including sample cells, the acoustic chamber,

and microphonic detector, were the original standard items supplied with the instrument. Air was used as the coupling gas. The spectrum of sample 1 was scanned from 2600 nm to 200 nm at a gain ratio of 5:1 using 2.0 mm slits (8 nm resolution) and referenced to carbon black. Sample 3 was scanned from 2600 nm to 200 nm at a gain ratio of 2:1 using 2.0 mm slits and also referenced to carbon black. The transmission spectrum of the UF_4 film on Al_2O_3 was obtained by placing the disk in the light path just before the acoustic chamber and running carbon black as a detector material. When this spectrum is referenced to the PAS spectrum of carbon black alone, the transmittance spectrum of the disk is obtained. The spectrum was scanned in the wavelength range of 2600 to 200 nm at a gain of 1:1 using 2.0 nm slits. Scan rates ranged from 50 nm/min to 200 nm/min, depending on the noise level.

The absorbance spectrum of the UF_4/KBr pellet was obtained using a Cary 17 spectrophotometer and a liquid helium dewar. Helium temperatures were achieved by pouring liquid helium directly over the sample. The spectrum was recorded for wavelengths from 2500 nm to 350 nm.

The various spectra are shown in Figures 1-4. The results of Conway[5] are included in Figure 1 for reference.

DISCUSSION

Conway[5] has described the spectrum of U^{4+} in CaF_4 using the prescription of Spedding[6] for Pr(IV) which, like U(IV), has an f^2 electronic configuration. He has obtained good agreement between experiment and this theory by selecting the Condon and Shorty ξ

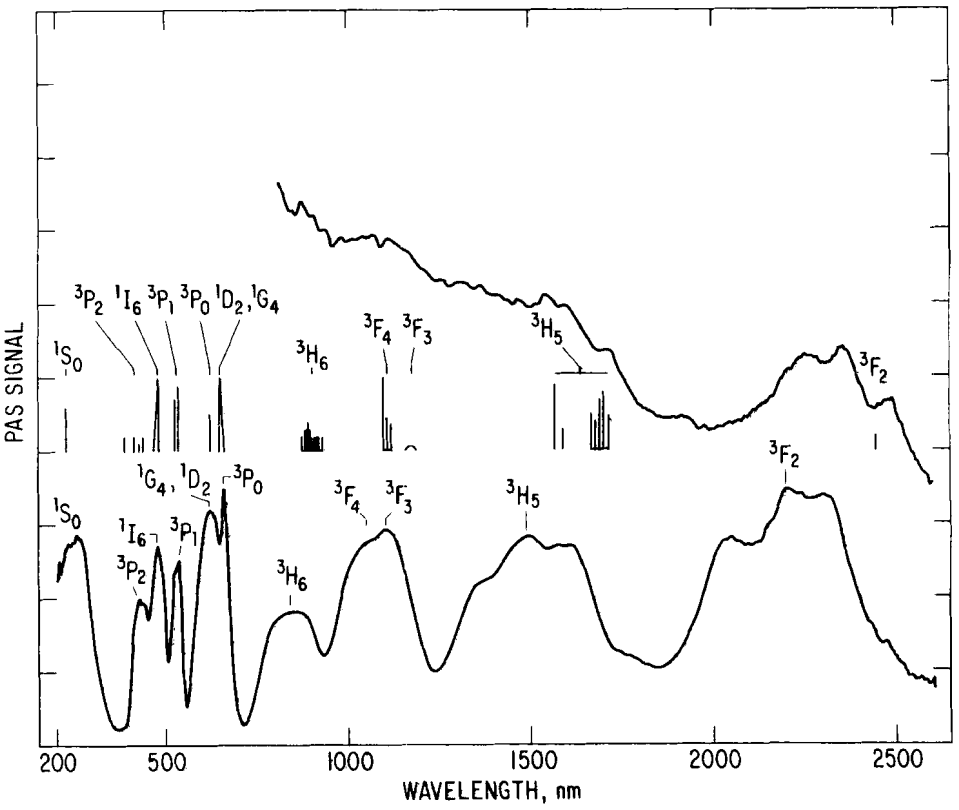

Figure 1. PAS spectra of Sample 1, and UO_2 powder (upper curve) with Conway's assignments for UF_2 in CaF_2.

parameter[10] to obtain best agreement. He has made two further points which should be noted: 1) the site symmetry of U^{4+} in CaF_2 is unknown, and 2) the absorption peak for this dilution system are much sharper than those observed in pure UF_4. No mention is made of the defects necessary to obtain charge neutrality which must be present in the fluorite lattice. Two possible point defects are interstitial fluorine or calcium vacancies. We suspect such defects may effect the absorption spectra of this solid dilution. While

the site symmetry of U^{4+} is not known, we expect the U^{4+} to be in a calcium site and therefore be eight-coordinate. Hecht and Gruber have comprehensively analyzed the absorption spectrum of a single crystal of UCl_4 at liquid helium temperatures. Electronic level assignments are in agreement with those of Conway for U^{4+} in CaF_2 with the following exception: the $^3P_1$ and $^1I_6$ overlap and the $^3F_3$ and $^3F_4$ bands also overlap. The higher site symmetry of the U^{4+} in UCl_4[11] made it possible for Hecht and Gruber to calculate the optical spectrum using a complete ligand field analysis. Their magnetic susceptibility data showed no antiferromagnetic behavior. Since the optical spectra of Conway for U in CaF_2 and Hecht and Gruber for UCl_4 are in general agreement with what we have found for UF_4, we have proceeded to use the methods of Conway to assign the electronic levels seen in UF_4.

The structure of UF_4 is monoclinic Ia/c8. The uranium atoms sites are eight-coordinate, distorted square antiprismatic with U-F bond distances ranging from 2.249 Å to 2.318 Å.[7] While such low site symmetry complicates group theoretical analysis, the small range of U-F bond lengths imply the crystal field effect differences between the U^{4+} in CaF_2 and that in UF_4 will be small, but still may cause some broadening of spectral features. This low symmetry is not due to distortions caused by the f^2 electron because $ThF_4(f^\circ)$ and $HfF_4(f^\circ d^\circ)$ have the same crystal structure.

It is probable that uranium-uranium magnetic interactions, either direct or superexchange via the fluorine, perturb the electronic levels and hence affect the absorption spectrum of UF_4. Several magnetic measurements[12-15] indicate that UF_4 has strong U-U interactions and is probably antiferromagnetic at low

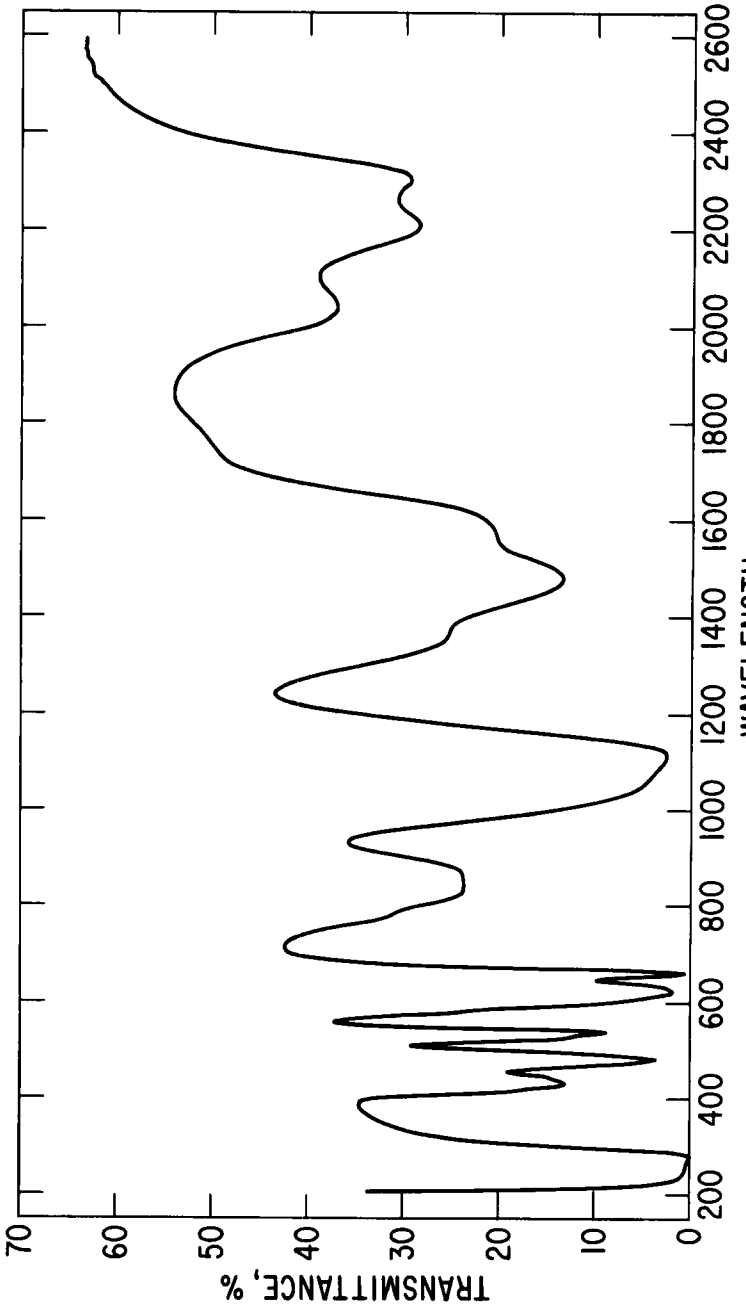

Figure 2. PAS %T of UF_4 film.

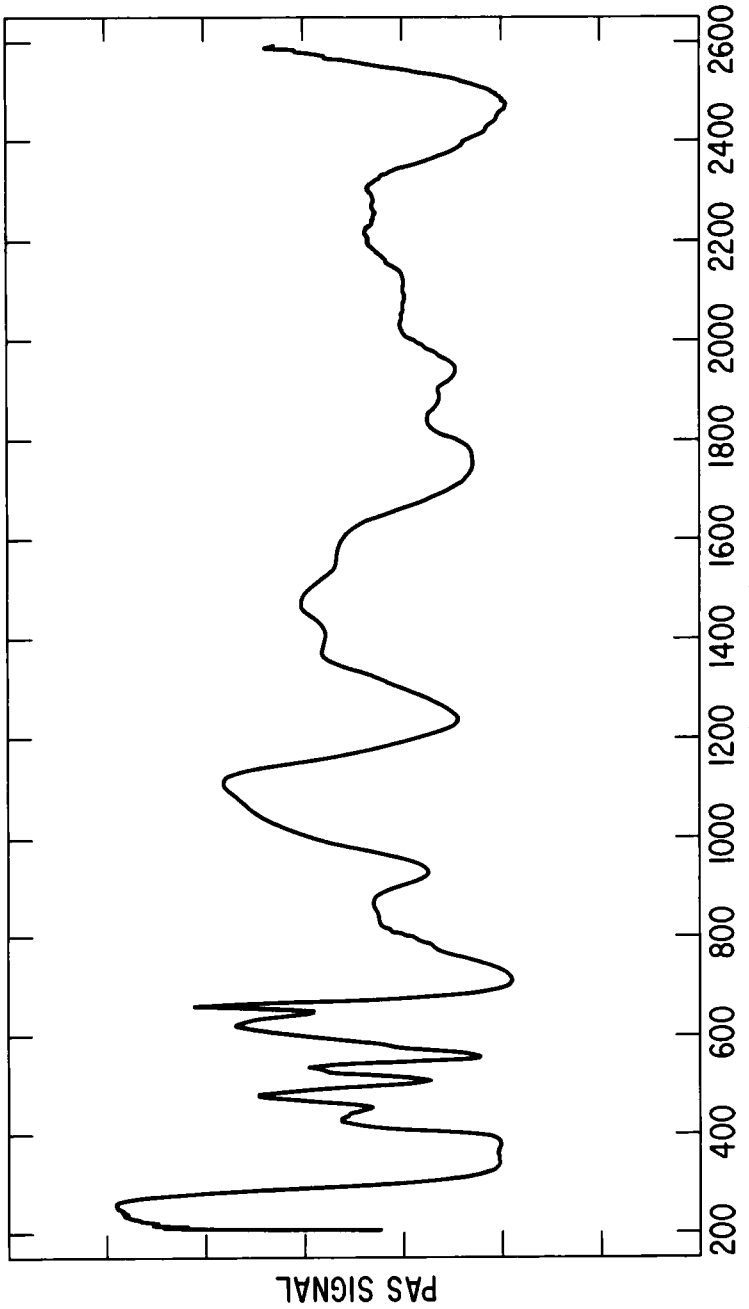

Figure 3. PAS of UF_4/KBr pellet.

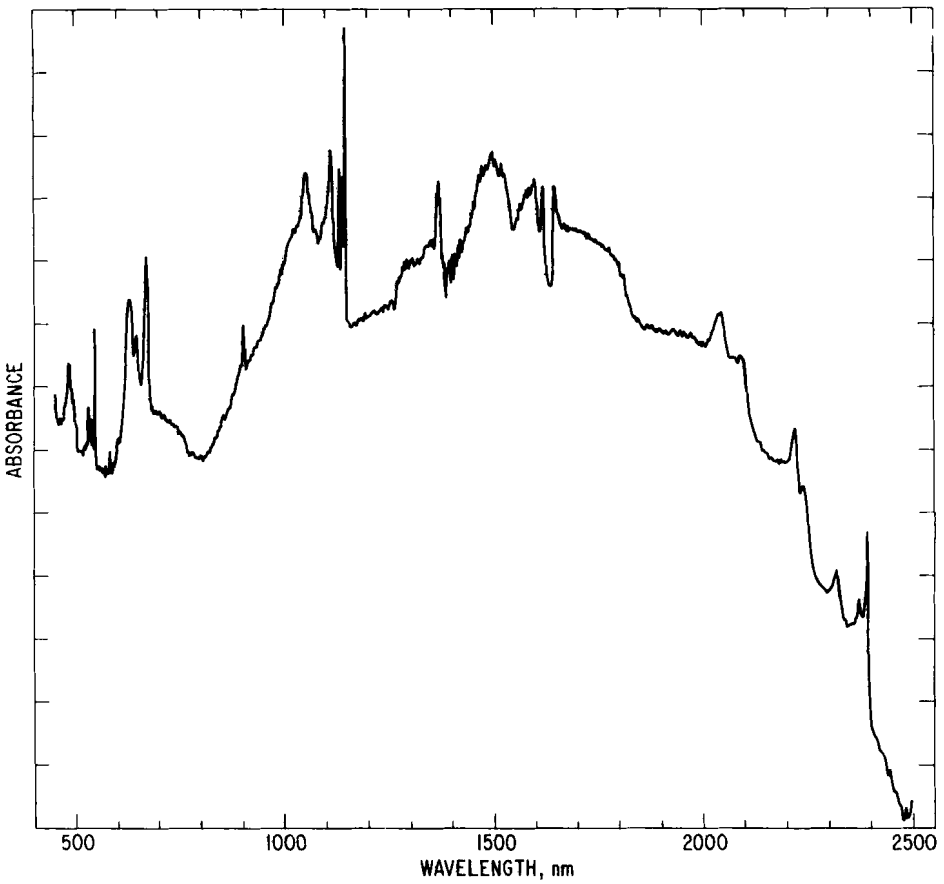

Figure 4. Cary 17 %T, Helium temperature spectrum of UF_4/KBr pellet.

temperatures. This implies two possible causes for the broad features seen in the absorption spectrum of UF_4 as compared to U^{4+} in CaF_2: 1) U-U magnetic interactions, and/or 2) low site symmetry causing J level splitting and therefore broadening into multiplet bands.

Figure 1 shows the room temperature PAS spectrum of UF_4. The spectral peaks reported by Conway are also shown and are in general agreement with the PAS peaks but slightly blue-shifted and much

broader. However, several features were more highly resolved than those observed in the study of U^{4+} in CaF_2. These additional splittings, for example in the $^3F_2$ peaks, are thought to originate in U-U interactions. The room temperature transmission spectrum of the UF_4 film on Al_2O_3 exhibited features similar to the PAS spectrum (Figure 2).

The liquid helium absorption spectrum of UF_4 in a KBr pellet (Figure 3) shows additional resolution compared to the room temperature bands. However, the number of resolved peaks was not consistent with the expected number of microstates for the given LS assignments. Furthermore, several energy levels are shifted relative to those found by Conway. The blue shift found for the $^3F_3$, $^3F_4$ and $^3H_5$ imply that ξ is larger in UF_4 than in U^{4+} in CaF_4. This leads to the crossing of the $^3P_0$, $^1D_2$ and $^1G_4$ levels and hence to the spectral assignments as shown. This argument is consistent with the shorter U-F bond distance observed in UF_4 than in U^{4+} in CaF_2. UO_2 also shows the same broad features as UF_4 (Figure 1). UO_2 has U^{4+} in a high symmetry (cubic) site and is known to be antiferromagnetic at low temperature. We feel this is evidence that the band broadening in UF_4 is also due to U-U interaction and not low site symmetry. The UO_2 spectrum is red-shifted compared to Ca^{4+} in UF_4, which is consistent with a longer u^{4+} anion interaction. The visible portion of the UO_2 spectrum is now shown, as it is complicated by free carrier absorptions.

FINAL REMARKS

The sharper features seen by Conway in U^{4+} in CaF_2 are most probably the result of reduced U-U interactions by dilution rather than the higher site symmetry of U in a Ca site. This agrees

with Conway's assumption that crystal field energy is small compared to spin-orbit energies. Helium temperatures spectra of UF_4 give resolved but wide multiplets indicating that thermal broadening is not the source of broad bands at room temperature.

We suggest several further experiments to help elucidate the optical spectrum and electronic structure of UF_4:

1) Low temperature magnetic susceptibility of UF_4 should be measured to help elucidate the strength and nature of U-U interactions in UF_4.

2) Optical and magnetic properties of the system $U_{1-x}Th_xF_4$ as a function of composition should be investigated. Since the structure of UF_4 and ThF_4 are the same, the U^{4+} and ThF_4 are the same, the U^{4+} spectrum is expected to sharpen with increasing x. the susceptibility experiments of Dawson[16] on this mixed system indicate that the U-U interactions do in fact decrease with increasing x.

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