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# Vibronic states of plutonium hexafluoride in the visible and near infrared spectral regions

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The entire absorption spectrum of  $PuF_6$  in the near IR and visible regions has been obtained at  $0.5 \text{ cm}^{-1}$  or higher resolution. A detailed analysis of the vibronic energy levels is presented and spectroscopic assignments of all observed transitions are made. The energy levels obtained from these spectroscopic measurements of the gas phase  $PuF_6$  molecule are the most accurate values available. A comparison is shown of our assignments and results with the matrix-isolation experiment and available theoretical studies.

# I. INTRODUCTION

The electronic structure of plutonium hexafluoride has been the subject of several experimental<sup>1-5</sup> and theoretical<sup>6-8</sup> investigations. Spectroscopically, plutonium hexafluoride exhibits an intense absorption in the ultraviolet region that is due to the charge-transfer process between the ligands and the central atom. In addition, several weak absorptions in the near infrared and visible regions are attributed to transitions among the spin-orbit coupled states resulting from the two 5 f electrons.

The first comprehensive gas phase absorption spectrum covering 4000–20 000 cm<sup>-1</sup> was recorded by Steindler and Gunther<sup>1</sup> in 1964. Walters and Briesmeister<sup>2</sup> refined the previous measurements in the wavelength region between 3000-9000 Å using a very long path length cell. In both cases the researchers used spectrometers with grating optics at spectral resolution of several wave numbers without resolving any vibrational components. Later, Kugel et al.<sup>3</sup> studied plutonium hexafluoride at a much higher resolution by an intracavity laser quenching technique. Recently, absorption and emission of matrix-isolated PuF<sub>6</sub> at 8 K have been reported by Dewey, Barefield, and Rice.<sup>4</sup> They assigned observed transitions below 17 000 cm<sup>-1</sup>. Finally, Kim et al.<sup>5</sup> studied the fine structure in the vibronic band near 800 nm. resolving Coriolis fine structure at a Doppler-limited resolution.

Theoretical computations were initiated by Koelling, Ellis, and Bartlett<sup>6</sup> on one-electron energy levels, using a relativistic Dirac–Slater model. Kugel *et al.* performed semiempirical ligand field calculations which include the effects of configuration interaction and spin–orbit coupling. Following this, Boring and Hecht<sup>7</sup> calculated the electronic structure and transitions employing a self-consistent field scattering wave approximation. Recently, Wadt<sup>8</sup> carried out an *ab initio* calculation of low lying 5 f-5 f excitations in PuF<sub>6</sub>. Most of the theoretical calculations are successful to various degrees of accuracy in explaining the general spectral features of plutonium hexafluoride. Spectroscopic assignments and refinements of the calculated energy levels have been made with the improvements in the recent experimental measurements.

In summary, the work by Steindler and Gunther and Walters and Briesmeister are low resolution and include no

analyses. The works by Kugel *et al.* and Kim *et al.* present high resolution data but only in a selected spectral range. The emission and absorption measurements by Dewey *et al.* are rough assignments with some degree of agreement in the general nature of the vibronic transitions. Using the matrixisolation technique to study vibronic transitions simplifies the spectra quite a bit; and although some fine details are lost in the matrix spectra, these experiments do complement gas phase studies very nicely.

In this paper, we report the entire absorption spectrum of  $PuF_6$  in the near IR and visible regions, obtained at very high sensitivity and at high resolution. Vibrational states are identified based on the ground state wave numbers, temperature-dependent intensity variations, and vibronic selection rules. Isotope shifts were measured in some cases in order to identify the specific vibrational modes. Spectroscopic assignments of all observed transitions are made and a comparison is shown of our assignments and results with available theoretical studies. We also present computergenerated spectral simulations, which aid in the understanding of the vibronic band contours.

## **II. EXPERIMENTAL**

Spectra of the gas phase plutonium hexafluoride were recorded using Fourier transform spectrometers (FTS) combined with a very long path length absorption cell.<sup>9</sup> Most of the spectra presented in this paper were obtained using a Bomem DA3.002 FTS at resolution of 0.5 cm<sup>-1</sup>; however, for a few scans, a Nicolet 20SX was used. This resolution was sufficient to resolve most of the vibrational components in vibronic bands, and in some cases rotational components were poorly resolved. A few of the spectral features required an increase in the resolution to  $0.05 \text{ cm}^{-1}$ . For the high resolution and weak transitions, in some cases several hours of scan time involving several hundred scans were required to completely record a spectral feature.

 $PuF_6$  samples were contained in a very long path length optical cell. The path length was in the range of 48–64 m. The sample gas pressures were kept at about 40 mTorr, seldom exceeding 60 mTorr. The sample size is limited in most cases by the vapor pressures in the cell. Spectra were obtained at room temperature and at lower temperatures (ap-

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0.6

proximately 220 K). At room temperature, the ground state population is 0.75%, while at 220 K, it is 4.4%.<sup>10</sup> Comparison between the spectra obtained at two different temperatures help distinguish the lowest energy transition from hot band transitions (transitions from vibrationally excited states).

PuF<sub>6</sub> samples were prepared by reacting PuO<sub>2</sub> or PuF<sub>4</sub> with F<sub>2</sub> at elevated temperatures (600 °C). Purification was done by cryodistillation prior to use in the 4 m cell. The purity of the PuF<sub>6</sub> was checked by running an infrared spectrum. No detectable impurities other than small amounts of CF<sub>4</sub>, HF, and SiF<sub>4</sub> were present. These impurities did not interfere with our measurements. Isotopic purity of PuF<sub>6</sub> samples was over 90% <sup>239</sup>PuF<sub>6</sub>. For isotopic shift measurements, we used PuF<sub>6</sub> samples enriched in <sup>242</sup>Pu.

All computer simulations of spectra were performed using a VAX computer.

## **III. RESULTS**

### A. Vibronic band assignments

In the near IR and visible spectral range,  $PuF_6$  exhibits four distinctly separate groups of absorption bands extending from 4000 to 20 000 cm<sup>-1</sup> where the charge-transfer bands begin. These clusters of absorption bands are located around 2.3  $\mu$ m, 1  $\mu$ m, 800 nm, and 560 nm. The absorption bands were correlated in part to electronic transitions among the spin-orbit coupled states of an octahedral field. For the most part, the transitions are enabled by the  $PuF_6$  molecular vibrations. Thus, each transition consists of several absorption bands corresponding to specific vibrational components. In addition, each absorption band consists of many overlapping hot bands, which determine the characteristic width of an absorption band.

For a given electronic transition, one can expect to discern a set of absorption bands associated with characteristic vibrational components. These absorption bands are arranged in such a way that on the lower energy side of the transition origin (designated hereafter as the 0–0 band) one sees absorption bands of a purely hot band nature and on the high energy side, absorption bands with the vibrational components of the excited electronic state. Thus,

$$E(\text{upper}) \leftarrow E(\text{lower}) + v_i, \tag{1}$$

 $E(\text{upper}) \leftarrow E(\text{lower}); \quad 0-0 \text{ band},$  (2)

$$E(\text{upper}) \leftarrow v'_i \leftarrow E(\text{lower}). \tag{3}$$

Here E(lower) and E(upper) refer to the lower and upper electronic states; and  $v_i$  and  $v'_i$  (i = 1,2,3,...,6) are the vibrational wave numbers of the corresponding states. In addition, one can have all possible combinations of vibrational combination and overtone bands. However, because of the selection rules governing vibronic transitions and the temperature dependent vibrational distribution, the number of the observed absorption bands is limited to several at most.

For most of the cases, one can make unique spectroscopic assignments of the gas phase spectrum based on the temperature-dependent behavior of the absorption features and the fundamental vibrational wave numbers of  $PuF_6$ . The

FIG. 1. Absorption spectrum of the 2.3  $\mu$ m region at 0.5 cm<sup>-1</sup> resolution.

temperature of the sample gas directly affects the population distribution. For PuF<sub>6</sub>, only the bending vibrations  $v_i$ (i = 4,5,6) and their combinations and overtones are significantly populated. The stretching vibrational frequencies are all high (>520 cm<sup>-1</sup>), and therefore their population is minimal. The relative intensities of the absorption bands in the above class (1), therefore, reflects the molecular population distribution at a given temperature while the absorption bands in class (2) and (3) are strictly determined by the vibronic transition probabilities. (Specific examples of this are reflected in the 800 nm region.) In the following, the spectral data and the assignments of the four transition groups are presented in increasing order of energy.

# 1. 2.3 μm region

For the lowest energy transitions, one expects three electronic states of symmetry,  ${}^{3}\Gamma_{4}$ ,  ${}^{2}\Gamma_{3}$ , and  ${}^{3}\Gamma_{5}$  in the 2.3  $\mu$ m regions.<sup>6</sup> Pure electronic transitions originating from the ground state  ${}^{1}\Gamma_{1}$  are electric-dipole forbidden in all three cases, while transitions to the  ${}^{2}\Gamma_{3}$  and  ${}^{3}\Gamma_{5}$  states are also magnetic-dipole forbidden. Figure 1 shows the spectrum of the 4000-6800 cm<sup>-1</sup> region, while Table I lists the assignments made for this region. This spectrum was obtained at 0.5 cm<sup>-1</sup> resolution and represents by far the weakest ab-

TABLE I. Observed transitions in the 2.3  $\mu$ m region.

Assignment	Frequency (cm <sup>-1</sup> )	
$\overline{{}^{3}\Gamma_{4}^{1}\Gamma_{1}+\nu_{6}}$	4401	
${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$	4575	
${}^{3}\Gamma_{4} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$	4748	
${}^{3}\Gamma_{4} + \nu_{3}' \leftarrow {}^{1}\Gamma_{1}$	5191	
${}^{2}\Gamma_{3} \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$	4668	
$^{2}\Gamma_{3} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$	5006	
${}^{3}\Gamma_{5} \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$	5641	
${}^{3}\Gamma_{5} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$	5991	
${}^{3}\Gamma_{5} + \nu_{3}' \leftarrow {}^{1}\Gamma_{1}$	6432	



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sorption band among the four groups. The band at 4575 cm<sup>-1</sup> has been assigned to the 0–0 band of the  ${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$ transition. This allows further assignment of the bands at 4401, 4748, and 5191 cm<sup>-1</sup> to the  ${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1} + v_{6}$ ,  ${}^{3}\Gamma_{4} + v_{6}'$  $\leftarrow {}^{1}\Gamma_{1}$ , and  ${}^{3}\Gamma_{4} + \nu'_{3} \leftarrow {}^{1}\Gamma_{1}$  transitions, respectively. Upon careful examination, one notices a shoulder band appearing at 4668 cm<sup>-1</sup>. This shoulder band is 338 cm<sup>-1</sup> apart from the band at 5006  $cm^{-1}$ . Based on theoretical calculations, the next excited state would be the  ${}^{2}\Gamma_{3}$  state. The bands at 4668 and 5006 cm<sup>-1</sup> are attributed to the  ${}^{2}\Gamma_{3} \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$  and  ${}^{2}\Gamma_{3} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$  transitions, respectively. This places the unobservable pure electronic transition at approximately 4837  $cm^{-1}$ . Appearing at slightly higher frequencies, there is another series of bands. The band at 5641  $cm^{-1}$  is separated  $350 \text{ cm}^{-1}$  from the band at 5991 cm<sup>-1</sup>. These bands have been assigned to the  ${}^{3}\Gamma_{5} \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$  and  ${}^{3}\Gamma_{5} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$ transitions, respectively. In this case, the unobservable pure electronic transition would be located at 5816 cm<sup>-1</sup>. Appearing 616  $\text{cm}^{-1}$  away from the location of the 0–0 band, there is a peak at  $6432 \text{ cm}^{-1}$ . This band has been assigned to the  ${}^{3}\Gamma_{5} + \nu'_{3} \leftarrow {}^{1}\Gamma_{1}$  transition. In order to further support the above assignments, this spectral region was examined at several temperatures. As expected, the bands assigned to hot bands decreased with decreasing temperature while the principal bands increased or sharpened up. With respect to the other small absorptions in Fig. 1, it is possible that they are due to étalon effects.

#### 2. 1 μm region

The absorption spectrum in the 1  $\mu$ m region is shown in Fig. 2, along with our assignments in Table II. Theory predicts<sup>6</sup> two electronic states,  ${}^{3}\Gamma_{4}$  and  ${}^{1}\Gamma_{1}$ , in this region. Once again, a transition to a  ${}^{3}\Gamma_{4}$  state is symmetry and magnetic-dipole allowed; however, a transition to a  ${}^{1}\Gamma_{1}$  state is symmetry and magnetic dipole forbidden. Looking at Fig. 2, one notices the spectrum contains two distinct types of band structure. The bands at 10 269 and 10 679 cm<sup>-1</sup> are narrower and have one-third the width of the other bands in the spectrum. Once again, the magnetic-dipole allowed  ${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$  transition shows a 0–0 band, which is located at

FIG. 2. Absorption spectrum of  $PuF_6$  in the 1  $\mu$ m region.

TABLE II. Observed transitions in the  $1 \,\mu m$  region.

Assignment	Frequency (cm <sup>-1</sup> )	
$3\Gamma_4 \leftarrow {}^1\Gamma_1 + \nu_4$	9 572	
${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$	9 595	
${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$	9 773	
${}^{3}\Gamma_{4} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$	9 945	
${}^{3}\Gamma_{4} + \nu_{4}' \leftarrow {}^{1}\Gamma_{1}$	9 971	
${}^{3}\Gamma_{4} + (\nu_{5}' + \nu_{6}') \leftarrow {}^{1}\Gamma_{1}$	10 141	
${}^{3}\Gamma_{4} + \nu_{3} \leftarrow {}^{1}\Gamma_{1}$	10 388	
${}^{1}\Gamma_{1} \leftarrow {}^{1}\Gamma_{1} + \nu_{4}$	10 269	
${}^{1}\Gamma_{1} + \nu_{4}' \leftarrow {}^{1}\Gamma_{1}$	10 679	

9773 cm<sup>-1</sup>. The band at 9595 cm<sup>-1</sup> can be assigned to the  $v_6$  hot band of this transition. Furthermore, the 9945 cm<sup>-1</sup> band with a shoulder at 9971 cm<sup>-1</sup> can be assigned to the  ${}^{3}\Gamma_{4} + v'_{6} \leftarrow {}^{1}\Gamma_{1}$  and  ${}^{3}\Gamma_{4} + v'_{4} \leftarrow {}^{1}\Gamma_{1}$  transitions, while the band located at 10 141 cm<sup>-1</sup> can be assigned to the  $(v_5 + v_6)$  combination. One also finds that the 9595 cm<sup>-1</sup> band is slightly wider toward the lower energy side than the other bands belonging to the same transition series. This broadening is caused by the adjacent unresolved  $v_4$  hot band at 9572 cm<sup>-1</sup>. Finally, one might note several small bands lying between the two distinct bands at 10 269 and 10 679 cm<sup>-1</sup>. The small band lying at 10 388 cm<sup>-1</sup> can be assigned to the  ${}^{3}\Gamma_{4} + v'_{3} \leftarrow {}^{1}\Gamma_{1}$  transition. With respect to the other small bands, it is possible that they are due to étalon effects.

As noted above, the second set of absorptions in the 1  $\mu$ m region consists of two peaks. Since the resulting state  ${}^{1}\Gamma_{1}$ is symmetry forbidden, the only allowed vibronic transitions would involve an  $F_{1u}$  component. This means that these two bands can only result from interaction with  $v_4$  and/or  $v_3$ vibrations. The separation between these two peaks is approximately 410 cm<sup>-1</sup>. This leaves two possible assignments. The first possibility is that the smaller peak at 10 269 cm<sup>-1</sup> is due to the  ${}^{1}\Gamma_{1} + \nu'_{4} \leftarrow {}^{1}\Gamma_{1}$  transition, while the larger band at 10 679 cm<sup>-1</sup> arises from the  ${}^{1}\Gamma_{1} + \nu'_{3} \leftarrow {}^{1}\Gamma_{1}$  transition. This would place the unobservable 0-0 band at 10 064  $cm^{-1}$ . The second possibility is that the band at 10 269  $cm^{-1}$ is due to a  $v_4$  hot band transition, while the 10 679 cm<sup>-1</sup> band arises from a  $v_4$  fundamental transition. This assignment would place the 0-0 band at 10 474 cm<sup>-1</sup>. If the smaller band is due to a hot band transition, it should decrease in intensity as the temperature of the sample gas is lowered. This particular absorption band is already narrow and does not show a significant temperature effect. However, an isotope shift of 0.17  $\pm$  (0.05) cm<sup>-1</sup> was measured between  $^{242}$ PuF<sub>6</sub> and  $^{239}$ PuF<sub>6</sub>. We conclude that the band at 10 269 cm<sup>-1</sup> is  $v_4$  and the larger band at 10 679 cm<sup>-1</sup> is the  $v'_4$  transition, thus favoring the second assignment.

#### 3. 800 nm region

Figures 3(a) and 3(b) shows two simulated spectra compared with the experimental spectrum of the 800 nm region. Three transitions,  ${}^{2}\Gamma_{3} \leftarrow {}^{1}\Gamma_{1}$ ,  ${}^{3}\Gamma_{5} \leftarrow {}^{1}\Gamma_{1}$ , and





FIG. 3. (a) and (b) Computer simulation of the 800 nm region compared with the experimental spectrum. (a) uses a model involving two transitions, while (b) uses a model involving three transitions. For both cases, the dotted line represents the experimental spectrum obtained while the solid line represents the computer-simulated spectrum.

 ${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$  are expected in this region.<sup>6</sup> A pure electronic transition is forbidden in the first two cases. A first interpretation of this portion of the spectrum is that the bands at 11 778, 12 101, and 12 566 cm<sup>-1</sup> are attributed to the  $v_6$  hot band and the  $v_6$  and  $v_3$  fundamentals of the  ${}^2\Gamma_3 \leftarrow {}^1\Gamma_1$  transition, respectively. This places the 0–0 band at 11 958  $\rm cm^{-1}$ . Furthermore, the bands at 11 935, 12 257, and 12 731  $cm^{-1}$ are due to the  $v_6$  hot band and  $v_6$ ,  $v_3$  fundamentals of the  ${}^3\Gamma_5$  $\leftarrow^{1}\Gamma_{1}$  transition, respectively. Therefore, the 0-0 band of this transition would be at  $12 \ 112 \ \text{cm}^{-1}$ . From this analysis, one can not identify absorption peaks belonging to the  ${}^{3}\Gamma_{4}$  $\leftarrow {}^{1}\Gamma_{1}$  transition. It is possible that some of the peaks may be overlapped with the absorption peaks assigned to the  ${}^{2}\Gamma_{3}$ and  ${}^{3}\Gamma_{5}$  states. The relative intensities of the absorption peaks assigned to  $v_3$  are markedly different than observed in the 2.3 and 1  $\mu$ m regions, which may suggest that indeed some of the intensity under the peaks at 12 566 and 12 731 cm<sup>-1</sup> is due to overlapping absorptions of the  ${}^{3}\Gamma_{4}$  state. Based on these observations, a second possible interpretation places the 0–0 band for the  ${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$  transition at about 12 588 cm<sup>-1</sup> and the  $v_6$  hot band,  $v_6$  and  $v_3$  fundamentals at 12 380, 12 703, and 13 168 cm<sup>-1</sup>, respectively.

We have simulated the observed spectrum based on two- and three-transition-state models [Figs. 3(a) and 3(b)]. The simulation results indicate that a two-state model is correct. A temperature dependence study indicates a hot band transition at 12 566 cm<sup>-1</sup>, which is also consistent with the above two-state model. Table III gives the final assignments made for the bands in the 800 nm region.

#### 4. 560 nm region

The spectrum of the 560 nm region is shown in Ref. 2. Theory suggests<sup>8</sup> that the first three transitions in this region are  ${}^{3}\Gamma_{4}$ ,  ${}^{2}\Gamma_{3}$ , and  ${}^{1}\Gamma_{1}$ . Based on this information only, assignments of the bands at 17 084, 17 786, and 18 432 cm<sup>-1</sup> have been made to these three transitions. We have not been able to obtain spectra at higher resolution than available in Ref. 2, so no further analysis was carried out.

## **B.** Spectral simulations

In the present work, we carried out two kinds of spectral simulations in order to analyze the observed vibronic bands. One objective is to simulate the absorption bands in each of the spectral regions as an additional check on the spectroscopic assignments made in the previous section. The other is to simulate individual absorption bands at an intermediate resolution using the ground state rovibrational band contours. In neither case do we use detailed molecular spectroscopic constants, derived from high resolution spectral analysis, as inputs for the spectral simulations.

For the low resolution spectral analysis, the positions of the absorption bands are completely determined by the vibrational frequencies of the lower (ground state) and upper electronic states. The vibrational frequencies of the ground electronic state of  $PuF_6$  are well known, but those of the excited state are not known. Once the transition frequencies are correctly identified, the present simulation yields information on the vibrational frequencies of the excited electronic states.

The transition probabilities of these absorptions are also unknown except for the 0–0 bands which are either present or absent, depending on whether they are magnetic dipole allowed or forbidden. Therefore, the relative intensities of the absorption peaks are adjusted to match the experimental spectrum at each peak position. Once adjusted in this way at a given temperature, the changes in the relative intensity as a function of temperature, when reproduced by simulation,

TABLE III. Observed transitions in the 800  $\mu$ m region.

Assignment	Frequency (cm <sup>-1</sup> )	
$\frac{1}{2\Gamma_3 \leftarrow {}^1\Gamma_1 + \nu_6}$	11 778	
${}^{2}\Gamma_{3} + \nu_{6}' \leftarrow {}^{1}\Gamma_{1}$	12 101	
${}^{2}\Gamma_{3} + \nu_{3}' \leftarrow {}^{1}\Gamma_{1}$	12 566	
${}^{3}\Gamma_{5} \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$	11 935	
${}^{3}\Gamma_{5} + \nu_{6}^{\prime} \leftarrow {}^{1}\Gamma_{1}$	12 257	
${}^{3}\Gamma_{5} + \nu_{3}' \leftarrow {}^{1}\Gamma_{1}$	12 731	

TABLE IV. Vibrational frequencies of PuF<sub>6</sub> electronic states.<sup>a</sup>

2.3 µm	1.0 µm	800 nm
616	615	610
•••	202	•••
•••	198	
172	172	145
	2.3 μm 616  172	2.3 μm 1.0 μm   616 615   ··· 202   ··· 198   172 172

\*Units are in cm<sup>-1</sup>. Uncertainties in  $v_i$  estimated to be about  $\pm 2$  cm<sup>-1</sup>. The ground state ( ${}^{1}\Gamma_{1}$ ) vibrational frequencies are 627, 524, 619, 201, 206, and 178 cm<sup>-1</sup> for  $v_1$  through  $v_6$  (Ref. 12) and used to obtain the difference frequencies where the 0–0 bands are absent.



FIG. 4. Partial spectrum of  $PuF_6$  in the 800 nm region at high resolution. Shows some of the spikey resolved features.

can provide strong support for the assignments of the absorption bands.

Table IV summarizes the vibrational frequencies of the electronic states. For all cases, we have not observed  $v_1$  and  $v_2$  so they are not included in the table. Furthermore, there is not enough information in the 560 nm region to include it in the table. The wave number differences among the various electronic states within each spectral region are small and do not warrant separate lists. In almost all cases, with the possible exception of  $v_4$ , we find that the vibrational frequencies of the excited electronic states are lower by several wave numbers than those of the corresponding ground states. We note here that the wave numbers of the bands were measured at the leading edge of the high energy side of the peaks whenever possible. In a few cases, it was very difficult to tell the exact position of the leading edge. This might explain why  $v_6$ in the 800 nm region is so much lower than the ground state frequency.

Computer generated spectral simulations were used extensively to aid in the analysis of the bands in the 800 nm region of the PuF<sub>6</sub> absorption spectrum. As mentioned previously, there are two possible models that can account for the band structure in this region. One model involves bands resulting from two transitions, while the other model involves three transitions. Figures 3(a) and 3(b) shows computer simulated absorption bands for a two-state vs threestate model, compared with the experimental spectrum. For these simulations, we ignore some of the "spikey" resolved features, which can be found as shown in Fig. 4, in the leading edges of some absorption bands. These are many overlapping rotational structures. Since the fine structure is ignored for this particular simulation, each band is represented by a Gaussian profile with a full width at half-maximum of 140 cm<sup>-1</sup>. The peak intensities were varied to reproduce the experimental spectrum. The positions of individual absorption peaks are displaced by the wave number differences from the 0-0 band position as shown in Table I.

As the spectral resolution improves, we start observing more resolved complex features on the high energy side of each absorption band. These are undoubtedly rovibrational structures. As in the case of the fundamental vibrations where the hot bands contribute to the overall rovibrational band shape, here the hot bands are now shifted to lower energy by the wave number difference between the ground state and the excited state. For example, for the  $v_3$  enabled absorption  $({}^{2}\Gamma_{3} + \nu'_{3} \leftarrow {}^{1}\Gamma_{1})$  at 800 nm, we have the usual *PQR* band structure with one of the hot bands of the nature  ${}^{2}\Gamma_{3} + (\nu'_{3} + \nu'_{6}) \leftarrow {}^{1}\Gamma_{1} + \nu_{6}$  now appearing to be shifted by the wave number difference  $(\nu_{6} - \nu'_{6})$  on the lower energy side. Only a few low lying states have significant population and show discrete absorption features. Because there are only a small number of states populated more than 1% at room temperature, superposition of all the hot bands represents the observed continuum absorption band. A computer simulation typically involves 250 states up to 3000 cm<sup>-1</sup> energy.

A computer simulation of such an overlapping absorption band assumes that a hot band rovibrational structure (i.e., PQR structure) is the same as the ground state structure. Previous results<sup>11</sup> support the validity of this assumption. The population of all available states is computed by the expression

$$P(E_i) = \rho(E_i) \exp(-E_i/kT)/Q_v.$$

Here  $\rho(E_i)$  is the densities of vibrational quantum states,  $Q_v$  is the vibrational partition function computed at temperature T, and k is the Boltzmann constant. Since only a limited amount of information is available on the vibrational frequencies of the excited states (Table IV), one further assumption was made. It was assumed that the spectral shift  $(v_i - v_0)$  is proportional to the energy of a particular vibrational state. Therefore,

$$\nu_i = \nu_0 - aE_i,$$

where a is a proportionality constant and  $v_0$  is the ground state transition frequency. Anharmonicities of vibrational states should be considered; however, these shifts are so small that their effect is negligible.

The intermediate resolution spectrum of the 800 nm region has been simulated quite well by the method described above. Combined with the high resolution spectrum reported previously by Kim *et al.*, this spectral feature is one of the best studied vibronic bands.

## **IV. DISCUSSION**

## A. Assignments and energy levels

The 5 f energy level in the octahedrally symmetric PuF<sub>6</sub> molecule splits into five spin-orbit coupled states. The

TABLE V. The f-f transitions and the resulting electronic states in  $PuF_6$ .

Excitation	Electronic states	
$1\gamma_{7u} \rightarrow 1\gamma_{8u}$	$\Gamma_{3g}(E_g), {}^{a}\Gamma_{4g}(T_{1g}), \Gamma_{5g}(T_{2g})$	
$1\gamma_{7u} \rightarrow 2\gamma_{7u}$	$\Gamma_{1g}(A_{1g}), \Gamma_{4g}(T_{1g})$	
$1\gamma_{7u} \rightarrow 2\gamma_{8u}$	$\Gamma_{3g}(E_g), \Gamma_{4g}(T_{1g}), \Gamma_{5g}(T_{2g})$	
$1\gamma_{7u} \rightarrow 1\gamma_{6u}$	$\Gamma_{2g}(A_{2g}), \Gamma_{5g}(T_{2g})$	

\*Double group notation with symmetry species in parentheses. Superscripts in the double group notation in the text refer to the state degeneracies.

ground state of  $PuF_6$  has two 5 f electrons in the lowest  $\gamma_{7u}$ level, and the remaining states are in increasing energy,  $\gamma_{8u}$ ,  $\gamma_{7u}$ ,  $\gamma_{8u}$ , and  $\gamma_{6u}$ . Table V summarizes one-electron transitions between the successive energy levels and the resulting electronic states.  $PuF_6$  displays an absorption spectrum in the visible and near IR regions which can be attributed to these specific transitions. Most of these transitions are vibronic in nature (pure electronic vibrations are forbidden for symmetry considerations). It is noteworthy that through the analysis of the vibrational components, aided by theoretical calculations, we are able to assign all the absorption features and thereby accurately determine the energy levels.

Several theoretical studies<sup>6-8</sup> have been performed investigating the excited electronic states of PuF<sub>6</sub> below 3 eV which arise from 5f - 5f transitions. Furthermore, Dewey et al. performed absorption and emission studies of matrixisolated  $PuF_6$ . It is important to realize that the theoretical calculations only provide approximate energy levels and the matrix experiments result in perturbations due to the matrix. Hence, there is a distinct advantage of measuring the gas phase spectra of  $PuF_6$  in order to obtain the most accurate results. Figure 5 is an energy level diagram which compares our results with other experimental and theoretical results. Using a simple one-electron picture, three excited states,  ${}^{2}\Gamma_{3g}$ ,  ${}^{3}\Gamma_{4g}$ , and  ${}^{3}\Gamma_{5g}$ , corresponding to the  $1\gamma_{7u}^{2} \rightarrow 1\gamma_{7u}^{\prime} 1\gamma_{8u}^{\prime}$ transition are predicted to occur around the 0.62 eV or  $2 \,\mu m$ region. Our spectral assignments are in very close agreement with Boring and Hecht<sup>7</sup>, who used a Ligand field without configuration interaction model. Kugel<sup>3</sup> and Wadt<sup>8</sup> predicted the  ${}^{3}\Gamma_{5}$  state to lie about 0.15 eV above our assignment of this state. Dewey, Barefield, and Rice<sup>4</sup> place the  ${}^{2}\Gamma_{3}$  state below the  ${}^{3}\Gamma_{4}$  state, which is not in agreement with our assignment or any of the theoretical assignments. The basis for distinguishing between these two states in the matrix experiments is the overlap of the absorption and emission spectra. For the  ${}^{3}\Gamma_{4} \leftarrow {}^{1}\Gamma_{1}$  transition, the absorption and emission spectra should overlap. The assignment of the 0--0,  $v_6$ , and  $v_6$ hot bands for the  ${}^{3}\Gamma_{4}$  transition are in close agreement, within 15  $cm^{-1}$ , of this gas phase work. However, this is the extent of the agreement in the 2.3  $\mu$ m region. The matrix work shows emission in the 3900-4400  $\text{cm}^{-1}$  region, which was assigned to transitions involving the  ${}^{2}\Gamma_{3}$  and  ${}^{3}\Gamma_{4}$  states; whereas, our gas phase spectra showed no absorptions in this region. This gas phase work showed absorptions in the 4600–5010 cm<sup>-1</sup> region which were assigned to transitions involving the  ${}^{2}\Gamma_{3}$  state. The other discrepancy between the



FIG. 5. Energy level diagram that compares our results with other experimental and theoretical results.

assignments of the matrix spectra and our gas phase spectra, in this region, is the energy of the  ${}^{3}\Gamma_{5}$  state. Dewey *et al.* assigned two bands at 5300 and 5744 cm<sup>-1</sup> to transitions involving the  ${}^{3}\Gamma_{5}$  state. Our spectra showed absorptions in the 5600–6500 cm<sup>-1</sup> region which were assigned to transitions involving the  ${}^{3}\Gamma_{5}$  state, but these bands were not detected in the matrix experiments. Although these two discrepancies between the matrix spectra and the gas phase spectra cannot be explained at this time, theory<sup>3,7,8</sup> supports the gas phase assignments.

For the 1.15 eV or 1.08  $\mu$ m region, the one-electron theory predicts  ${}^{1}\Gamma_{1g}$  and  ${}^{3}\Gamma_{4g}$  electronic states, corresponding to the  $1\gamma_{7u}^{2} \rightarrow 1\gamma_{7u}^{2}2\gamma_{7u}$  transition. Once again, our results are in best agreement with Boring and Hecht, although they place the  ${}^{1}\Gamma_{1}$  state approximately 0.1 eV above where our assignment is made. Wadt's calculation, involving relativistic effective core potential (RECP), inverts the ordering the  ${}^{3}\Gamma_{4}$  and  ${}^{1}\Gamma_{1}$  states. Results of the matrix experiment found the  ${}^{3}\Gamma_{4}$  state to lie below the  ${}^{1}\Gamma_{1}$  state which is in agreement with our results. Furthermore, almost all of the assignments made in the matrix, for this region, were within 15 cm<sup>-1</sup> of our assignments for the gas phase spectra. In fact, only two minor discrepancies existed between the matrix and gas phase spectra in this region. The first is that we observed a small absorption at 10 388 cm<sup>-1</sup> which is assigned to the  $\nu_{3}$  hot band for the  ${}^{3}\Gamma_{4}$  transition. The matrix experiment showed no sign of a band in this region; however, it could have been too weak to have been observed in the matrix. The second difference in the two experiments is that the matrix experiment only showed one band which could be assigned to a transition involving a  ${}^{1}\Gamma_{1}$  state; therefore, an assignment of this band could not be made. However, this band occurs within 2 cm<sup>-1</sup> of the band which we assigned to the  $v_{4}$  hot band transition of the  ${}^{1}\Gamma_{1}$  state.

The one-electron picture begins to break down with the next set of excited states,  ${}^{1}\Gamma_{1g}$ ,  ${}^{1}\Gamma_{2g}$ ,  ${}^{2}\Gamma_{3g}$ , (2) ${}^{3}\Gamma_{4g}$ , and (2)<sup>3</sup> $\Gamma_{5g}$ , corresponding to the  $1\gamma_{7u}^2 \rightarrow 1\gamma_{8u}^2$  transition, which are predicted to lie near 1.24 eV or the 800 nm region. Our results show two excited states,  ${}^{2}\Gamma_{3}$  and  ${}^{3}\Gamma_{5}$ , in the 1.2 eV region, with the remaining states higher than 2 eV. These results are in close agreement to those presented by Dewey et al. and Boring and Hecht. In fact, the assignments made in the matrix experiment were within  $25 \text{ cm}^{-1}$  of the assignments made in this work. Once again, Wadt's RECP model inverted the  ${}^{2}\Gamma_{3}$  and  ${}^{3}\Gamma_{5}$  states; however, it did predict the remaining states to lie higher than 2 eV. Finally, Kugel et al. postulated that the regular fine structure of the bands in the 800 nm region resulted from the presence of numerous rotational heads. The work presented here shows that these bands are vibrational hot bands, each having a poorly resolved POR-type rotational structure. This fact is supported by several pieces of evidence. First, we have performed spectral simulations, as discussed previously, to demonstrate this point. Second, there is the high resolution work that was reported in Ref. 5. Third, as a test case, we integrated the area under the 780 and 790 nm band regions. The area under the curve representing the PQR structure is roughly 4% for the 790 nm region and 6% for the 780 nm region, which does match, within experimental error, the ground state population at this temperature.

Finally, the remaining states lie higher than 2 eV and our spectrum did not have enough information to perform any real analysis in this region.

#### **B. Vibronic band intensities**

The  $PuF_6$  vibronic bands reported in this paper are all very weak. Our present experimental setup, which combines a long path length cell and FTS, enormously enhances the sensitivity over conventional methods, typically by a factor of  $10^3$ . This enabled us to record most of the transitions at a relatively high resolution. In addition, the wide spectral coverage afforded from the present method allows comparison of the relative transition strengths among the observed vibronic band regions.

The absolute transition strengths (S) were determined by integrating the area enveloped by the absorption bands, using the expression

$$S=\frac{1}{Nl}\int\ln\left(\frac{I_0}{I}\right)d\nu,$$

where N is the number density and 1 is the optical path length. The transition strengths are calculated and summarized in Table VI. Also, a comparison is made in Table VI between our results and those of the matrix-isolation experi-

TABLE VI. Transition strengths in PuF<sub>6</sub>.

Region	·	Transition strength	l
	(cm) <sup>a</sup>	(km/mol) <sup>a,b</sup>	(km/mol)°
2.3 μm	2.17×10 <sup>-18</sup>	11.58	6.62
$1 \mu m$	1.07×10 <sup>-17</sup>	32.86	41.00
800 nm	1.07×10 <sup>-17</sup>	32.86	60.00
560 nm	4.26×10 <sup>-17</sup>	132.48	

\*Our work.

<sup>b</sup>Calculation performed as shown in Ref. 12.

<sup>c</sup> Reference 4.

ments. We find that the transitions strengths decrease for the four regions in the order of 560 nm  $> 1 \,\mu\text{m} = 800 \,\text{nm} > 2.3 \,\mu\text{m}$  region.

Furthermore, within a particular band system, our experiments showed that the intensities of the hot bands are much more sensitive to variation in temperature than are the intensities of the principle bands. This is because the number of molecules in the various vibrationally excited levels of the ground electronic state reflects the molecular distribution at a given temperature, while the intensities of the principal bands are determined by the overlap integral of the vibrational eigenfunctions of the upper and lower states for the bands.

Finally, one might note that for the bands in the 2.3  $\mu$ m and 1  $\mu$ m systems, the intensity of  $\nu'_6 > \nu_6 > \nu'_3$ , while for the bands in the 800 nm region, the intensity of  $\nu'_3 > \nu'_6 > \nu_6$ . This change of relative intensities between the  $\nu'_6$  band and the  $\nu'_3$  band is only a reflection of the difference in the vibronic transition probability.

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