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p-*f* and *f*-*f* transitions of $U^{6+}O_5F$ and $U^{5+}O_5F$ centers in LiF

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An overall analysis of the energy levels of $U^{6+}O_5F$ and $U^{5+}O_5F$ centers of C_{4v} symmetry in LiF is presented. First, the experimental energies of the fine-structure lines of seven *p*-*f* transitions of the prominent $(U^{6+}O_5F)^{5+}$ center of C_{4v} symmetry are determined from well resolved absorption spectra in the UV range and from polarized emission and excitation experiments in the range 18 000–40 000 cm^{-1}. Second, a comparison with the *f*-*f* energy levels of U^{5+} previously observed in x or γ irradiated UO_5F centers shows that the energies of the *p*-*f* transitions of U^{6+} can be approximately accounted for by shifting the energies of the *f*-*f* transitions of U^{5+} by $\Delta = 19\,493$ cm^{-1}, Δ representing the energy difference between the center of gravity of the fine-structure levels of the first excited level and the fundamental level of the configuration $5f^0$. Finally, an analysis of the fine-structure lines associated to the *p*-*f* transitions and a comparison with the relativistic electronic structures of configurations $5f^0$ and $5f^1$ of cubic molecules UF_6, UF_6^-, and NpF_6 are made in order to determine which *p* and *f* orbitals are associated to the observed *p*-*f* transitions of U^{6+}.

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I. INTRODUCTION

The experimental and theoretical analyses of the electronic structure of actinides such as uranium, neptunium, and plutonium has long attracted much attention.[1–4] In the case of very strongly ionized actinides in molecules, many studies have been performed on configuration $5f^0$ of U^{6+} in octahedral molecules UF_6,[1–3] on configuration $5f^1$ of U^{5+} in UF_6^-[4] and NpF_6,[1] and on configuration $5f^2$ of PuF_6.[1] Concerning the theoretical models, relativistic effects and configuration interactions are of primary importance to calculate the energy levels of heavy atoms (see, for example, a recent calculation on lawrencium and lutetium in Ref. 5), and to determine the energy levels of molecules involving heavy ions such as UF_6,[1,2] NpF_6,[1] and PuF_6.[1]

In the case of $U^{6+}O_5F$ and $U^{5+}O_5F$ centers in LiF the molecular models are much more complex than for octahedral molecules such as UF_6 and NpF_6 for two main reasons (i) the site symmetry is C_{4v} instead of O_h (see the structure of the UO_5F centers in Fig. 1) and two different nearest ligands F and O intervene, thus considerably complicating the model for the molecule and (ii) it is necessary to account for the influence of the crystal on the molecular orbitals in order to determine the multielectronic wave functions and, in the case of U^{6+}, the fine-structure of the charge-transfer transitions (CTT). Therefore, for U^{6+} centers, it would be very interesting to determine from experiments the symmetry of the fine-structure lines associated to the CTT's and the orbitals involved in the CTT's in order to check the validity of the molecular models.

In molecular models involving strongly ionized ions of transuranium elements (see Refs. 1–4), a CTT is a transition associated to the internal transfer of one electron of a molecular center from filled *p* orbitals of the ligands to empty *f* orbitals of the transuranium element. More specifically, in the case of U^{6+} in the UO_5F molecular center, the fundamental state (formally denoted $5f^0$) is filled, and the *p*-*f* CTT's are due to the promotion of one electron from filled molecular orbitals which are predominantly built from the *p* orbitals of fluorine and oxygen to empty molecular orbitals which are predominantly $5f$ orbitals of uranium. When adding one electron to the $U^{6+}O_5F$ molecular center, this electron is located on the $5f$ orbital at lower energy and the formal configuration becomes $5f^1$.

The relativistic Dirac-Slater (DS) model of Onoe *et al.*[3] for octahedral molecules UF_6, and the relativistic DS model of Koelling, Ellis, and Bartlett[1] for UF_6 and NpF_6 are of particular interest since they correctly account for many optical levels of the configurations f^0 and f^1. They will be used as a guide to analyze the optical energy levels of $U^{6+}O_5F$ and $U^{5+}O_5F$ centers in LiF. (In fact, we propose a method analogous to that developed for iron group ions in crystals, in particular, for d^5 ions, where the multiplets and the fine-structure lines are determined from experiments and where the crystal-field model, which approximately accounts for few multiplets at lower energy only,[6] is used as a guide.

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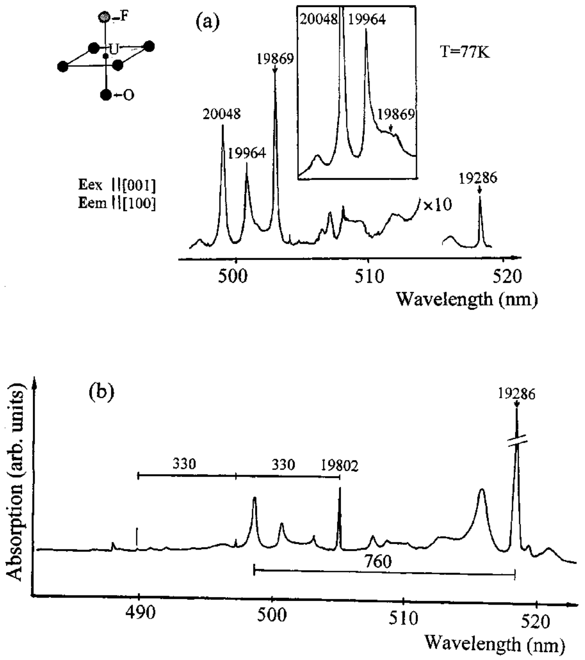

FIG. 1. $U^{6+}O_5F$ centers in LiF. (a) Excitation spectrum of the emission line at 527.8 nm (18 947 cm^{-1}) and polarization effect for the line at 503.3 nm (19 869 cm^{-1}) for $E_{ex}||E_{em}$ and, see inset, for $E_{ex}\perp E_{em}$. The zero phonon lines are marked by an arrow. Two zero phonon lines appear at 19 286 and 19 869 cm^{-1}. The structure of the UO_5F centers is given to the left. The U-F bond is along the cubic [100], [010], and [001] axes of LiF, $T = 77$ K. (b) Absorption spectrum of LiF-U_3O_8 in the range 19 150–20 620 cm^{-1}, at $T = 77$ K. One zero phonon line of the prominent center appears at 19 286 cm^{-1}. As shown in Sec. II B, the line at 19 802 cm^{-1} is due to another uranium center. The line at 19 286 cm^{-1} is 4.5 more intense than the line at 19 802 cm^{-1}. The horizontal axis gives the wavelength in nm. The energies of the lines are in cm^{-1}.

Molecular models are then elaborated to account for well-defined experimental results.[7])

The molecular UO_5F center in LiF is of particular interest since several CTT's of U^{6+} show a fine-structure which gives the symmetry of the involved molecular orbitals. Furthermore, a comparison with the *f-f* transitions of U^{5+} obtained by x or γ irradiation can be made, thus permitting a direct comparison of the energy levels associated to the two ionization states.

Early experiments including the uniaxial stress effect,[8] the external electric-field effect,[9] and polarization effects on electric and magnetic dipole transitions[10] have been performed on prominent optical lines appearing in the visible region of the $U^{6+}O_5F$ center.

Electron paramagnetic experiments performed on U^{5+} created from x or γ irradiation have permitted to study numerous U^{5+} centers appearing in LiF and to unambiguously determine the structure of the prominent $U^{5+}O_5F$ center which shows a hyperfine coupling with only one fluorine ion.[11]

A systematic study of the absorption, emission, and excitation spectra of the optical energy levels of the $U^{5+}O_5F$ center has permitted to determine the energy levels of U^{5+} and to elaborate a parametric model to account for the energy levels and the Landé *g* factors of the fundamental level.[12]

Polarized excitation spectra of U^{6+} centers in the visible and near ultraviolet (UV) region have permitted an unambiguous determination of the symmetry of several fine-structure lines of the prominent UO_5F center.[13,14]

Very recently, the absorption spectra of U^{6+} centers in LiF and NaF have been determined by Pustarov *et al.*[15] up to 40 eV. Amongst the numerous experimental lines, they observed one absorption line in the UV region which, due to the limited range of our spectrometer, was lacking in our absorption spectra of U^{6+} and therefore in our model which was based on the comparison of seven *p-f* CTT's of U^{6+} with the seven *f-f* energy levels of the f^1 configuration of U^{5+}.

Up to now the optical levels of $U^{6+}O_5F$ centers in LiF have never been compared with the optical levels of $U^{5+}O_5F$ centers reported in Ref. 12. Thus, the aim of this paper is (i) to compare the energy levels of U^{6+} and U^{5+} centers in LiF, (ii) to present an overall analysis for the *p-f* CTT's of U^{6+} which appear in the visible and near UV region, (iii) to present an overall analysis for the *f-f* transitions of U^{5+} which appear in the visible and near infrared region, and (iv) to elaborate a common molecular model for these centers.

In Sec. II, the energy levels of the $U^{6+}O_5F$ center in LiF are determined from well resolved absorption spectra, and from previous polarized emission and excitation experiments in the visible and UV region. It is shown in Sec. III that the energy levels of U^{6+} can be approximately obtained by simply translating those of U^{5+}. In Sec. IV, the symmetry of the molecular orbitals of the *p-f* CTT's of U^{6+} is deduced from the symmetry of the orbitals of the *f-f* transitions of U^{5+} and the symmetry of the fine-structure levels of the *p-f* CTT's. Then, the molecular orbitals are compared with those of the molecules UF_6, UF_6^-, and NpF_6 as given by the relativistic DS models.[1–4]

II. EXPERIMENTS

A. Samples and apparatus

The LiF crystals doped with U_3O_8 were grown by the Kyropoulos method at Argonne National Laboratory. The initial concentrations are 80 g LiF–0.2 g U_3O_8, 80 g LiF–0.08 g U_3O_8, and 80 g LiF–0.04 g U_3O_8.

The absorption experiments were performed with a Cary 14 spectrometer.

For excitation experiments performed in the limited range 19 800–20 100 cm^{-1}, a krypton laser coherent radiation CR 3000 K was used to excite a dye laser CR 3500 with Coumarin 30. The output power from the dye lasers was about 20 mW, the linewidth being 0.1 Å. The emission lines were analyzed with a Jobin Yvon spectrometer HRS 2 operating in the visible region (1200 lines per mm grating, blazed at 5500 Å).

B. *p-f* transitions of $U^{6+}O_5F$ centers in LiF

Since several uranium centers exist in LiF, absorption experiments were performed on crystals having the initial concentrations given in Sec. II A in order to determine the absorption lines and bands associated to the prominent uranium center. In fact, when increasing the concentration in uranium, new absorption lines appear. For the highest initial concentration of 80 gr. LiF–0.2 gr. U$_3$O$_8$, many new centers are created so that numerous new absorption lines and at least ten new emission lines clearly appear in the visible region. Fortunately, these new lines are sharp, at liquid-nitrogen temperature, and easily recognizable on the spectra. Furthermore, absorption experiments performed on crystals with the initial concentrations given in Sec. II A have shown that the new centers have different growing rates in terms of the initial concentration. Practically, the lines observed in the absorption spectra can unambiguously be associated either to the prominent center or to other centers. Of course, the absorption, excitation, and emission experiments were performed on the same crystal.

We will now present an overall view of the absorption and excitation spectra which permitted us to determine the energy levels of the U^{6+} centers in LiF. For the chosen concentration, only one strong and sharp (at liquid-nitrogen temperature) emission line is associated to the prominent center. The polarized excitation spectra represented in Fig. 1(a) have already been published.[13] Polarized excitation spectra of the emission line of the prominent uranium center, in the energy range of Figs. 1 and 2, have been published by Srinivasan *et al.*[14] However, the absorption spectra reported here show a much better resolution in the UV range [Fig. 2(c)] and, therefore, show new sharp lines which permitted us to define the zero phonon lines and phonon assisted lines in the UV range. Furthermore, several lines due to another uranium center are observed in our absorption spectra.

The selected absorption spectra presented here correspond to the lowest concentration in uranium oxide (80 g LiF–0.04 g U$_3$O$_8$). Figures 1 and 2 represent parts of a single absorption spectrum. Most of the absorption lines are associated to the prominent UO$_5$F center whose structure is given in Fig. 1. However, even for this low concentration, several weak lines appearing in the excitation, absorption, and emission spectra are due to other uranium centers. These other centers show growing rates in terms of concentration which differ from the growing rate of the prominent center.

We will first briefly recall the excitation experiments previously performed in the range 19 200–20 100 cm^{-1}.[13] Polarized excitation spectra in the visible region of the very strong emission line at 527.8 nm (18 947 cm^{-1}) are presented in Fig. 1(a). An inset in Fig. 1(a) shows the polarization effects on the line at 503.3 nm (19 869 cm^{-1}). By measuring the polarization effect by the ratio R of the amplitude of the line when the electric field $\mathbf{E}_{ex}$ of the excitation light is perpendicular to the electric field $\mathbf{E}em$ of the emission light to the amplitude of the emission line when $\mathbf{E}_{ex}$ is parallel to $\mathbf{E}_{em}$, we obtained $R=0$ for the line at 503.3 nm (19 869 cm^{-1}).

The excitation spectrum (not represented) of the emission line at 518.5 nm (19 286 cm^{-1}) is identical to that of the line at 527.8 nm (18 947 cm^{-1}) except for the polarization effects for the line at 503.3 nm (19 869 cm^{-1}). Polarization experiments performed on the two lines at 518.5 nm (19 286 cm^{-1}) and 503.3 nm (19 869 cm^{-1}) show that $R=\infty$. Polarization experiments performed on the two lines at 527.8 nm (18 947 cm^{-1}) and 518.5 nm (19 286 cm^{-1}) give $R=5$. From these experiments, it has been shown that the lines at 527.8 nm (18 947 cm^{-1}), 518.5 nm (19 286 cm^{-1}), and 503.3 nm (19 869 cm^{-1}) are of symmetry Γ_2, Γ_1, and Γ_5 respectively.[13]

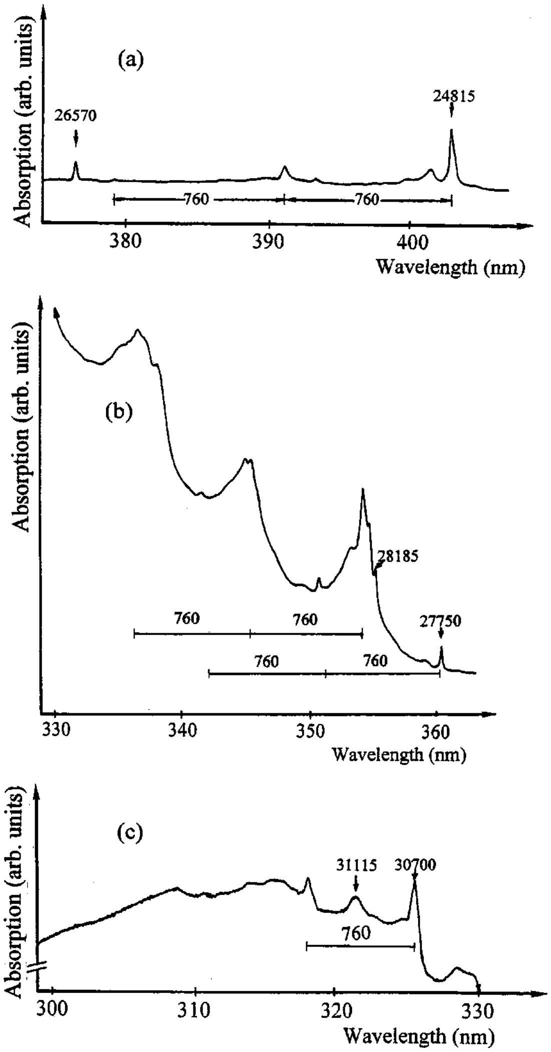

FIG. 2. U^{6+}O$_5$F centers in LiF. Absorption spectra in the range 24 800–33 300 cm^{-1} at $T=77$ K. The zero phonon lines are marked by an arrow. In (a), two zero phonon lines appear at 24 815 and 26 580 cm^{-1}. In (b), two zero phonon lines appear at 27 760 and 28 185 cm^{-1}. In (c), two zero phonon lines appear at 30 700 and 31 115 cm^{-1}. The horizontal axis gives the wavelength in nm. The energies of the lines are in cm^{-1}. In Fig. 2(c), the spectrum has been translated vertically with respect to the other absorption spectra.

An absorption spectrum in the visible region is presented in Fig. 1(b). The absorption and excitation spectra differ by the presence of a relatively strong absorption line at 505.0 nm (19 802 cm^{-1}) with one and two phonon assisted lines, the energy of the phonons being of $\hbar\omega=330$ cm^{-1}. Emission experiments performed on this line show that it is an excitation line of an emission line at 513.6 nm (19 470 cm^{-1}) which is not observed in absorption spectra. These emission experiments show that the line at 505.0 nm (19 802 cm^{-1}) is not an excitation line of the lines at 518.5 nm (19 286 cm^{-1}) or 527.8 nm (18 947 cm^{-1}). Excitation experiments performed on the line at 513.6 nm (19 470 cm^{-1}) confirm that, in the visible region, this line is excited by the line at 505.0 nm (19 802 cm^{-1}). However, optical and electron-paramagnetic-resonance experiments performed by Lupei, Lupei, and Ursu[11] on LiF strongly doped with uranium have shown that the emission line at 513.6 nm (19 470 cm^{-1}) and the corresponding excitation lines are not due to the prominent $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center but are to be associated to another uranium center (center II in Ref. 11).

Other lines associated to the configuration $5f^0$ are shown in Fig. 2. This figure represents the absorption spectra in the range 300–405 nm (24 590–33 330 cm^{-1}). No line is observed in the range 485–405 nm (20 620–24 690 cm^{-1}). In Fig. 2(a), the lines at 403.0 nm (24 815 cm^{-1}) and 376.4 nm (26 570 cm^{-1}) are associated to the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center. One and two phonons assisted line with $\hbar\omega = 760\ \mathrm{cm}^{-1}$ of the line at 403.0 nm (24 815 cm^{-1}) are observed. In Fig. 2(b) the lines at 360.4 nm (27 750 cm^{-1}) and 354.8 nm (28 185 cm^{-1}) are associated to the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center. One broad band appears at 28 260 cm^{-1}. One and two phonon assisted lines and bands, with $\hbar\omega = 760\ \mathrm{cm}^{-1}$, are clearly identified on the spectrum. In Fig. 2(c), the lines at 325.7 nm (30 700 cm^{-1}) and 321.4 nm (31 115 cm^{-1}) are associated to $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ centers. One phonon assisted line with $\hbar\omega = 760\ \mathrm{cm}^{-1}$ is observed.

Polarized excitation experiments and magnetic circular dichroism experiments performed in the visible and near UV range by Srinavasan *et al.*[14] have clearly shown that the lines at 403.0 nm (24 815 cm^{-1}) and 376.4 nm (26 570 cm^{-1}) are excitation levels of symmetry Γ_5 of the point group C_{4v} of the fluorescent level at 527.8 nm (18 947 cm^{-1}). They also observed excitation bands in the range 27 750–32 000 cm^{-1} with low resolution. By comparing these bands with the much more detailed absorption spectra of Fig. 2(c), it appears that the line at 360.4 nm (27 750 cm^{-1}) is of symmetry Γ_1 and that lines near 355.0 nm (28 170 cm^{-1}) are of symmetry Γ_5. Several broad bands observed by Srinavasan *et al.*[14] in the range 29 000–30 700 cm^{-1} are phonon assisted lines as shown in Fig. 2(b). Furthermore, they have observed a broad line of symmetry Γ_5 at 325.0 nm (30 770 cm^{-1}).

As it will be seen in the following section, one energy level near 37 000 cm^{-1} was predicted by the proposed model but not observed in our experiments due to the limited spectral range of our spectrometer.

Fortunately, experiments have recently been performed in the UV and far UV range on LiF and NaF doped with uranyl nitrate and copper fluoride by Pustarov *et al.*[15] For the authors, the structure of the prominent uranium center is that of the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center. Excitation spectra of a band at 2.38 eV (19 200 cm^{-1}) have been recorded in the range 5–40 eV. Several excitation lines have been observed below the gap of LiF at 3.84 eV (30 970 cm^{-1}), 4.84 eV (39 040 cm^{-1}), 5.44 eV (43 880 cm^{-1}), 6.65 eV (56 640 cm^{-1}), 9.40 eV (75 820 cm^{-1}), 10.40 eV (83 890 cm^{-1}), and 11.24 eV (90 660 cm^{-1}). Given the poor resolution of the spectra, it is not possible to determine whether the observed lines are phonon assisted lines or not. However, given the large energy separation between the observed lines, we will simply associate the lines to the energy levels of uranium. The band at 19 200 cm^{-1} approximately corresponds to the emission at 18 947 cm^{-1}. The band at 30 970 cm^{-1} probably corresponds to the line observed at 30 700 cm^{-1} in our absorption experiments. The line at 39 040 cm^{-1} is of particular interest since it is probably the missing line of the model developed in the following section.

III. COMPARISON WITH THE *f-f* TRANSITIONS OF $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ CENTERS IN LiF

The energy levels of the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ and $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ centers are presented in Fig. 3.

Concerning the energy levels of U^{5+} centers, it must be noted that (i) the absorption experiments reported in Ref. 12 have clearly shown that only few U^{6+} centers can be transformed into U^{5+} centers by x or γ irradiation (not by visible or UV light) so that both U^{6+} and U^{5+} centers are observed in the same sample; (ii) excitation experiments of the emission line at 4778 cm^{-1} [see Fig. 3(c)] were carefully performed in the IR, visible, and near UV region in order to determine all *f-f* transitions of the U^{5+} center; and (iii) no line of U^{6+} centers was found to be an excitation line of U^{5+} centers. It can be noted here that the CTT's defined in the Introduction as intramolecular transitions differ from the CTT's used to explain some transitions associated to different ionic charges and bound holes of iron group ions as Fe^{3+} and Fe^{2+}.[16,17] CTT's involving the U^{5+} and U^{6+} centers, in the sense of Refs. 16 and 17, have not been observed.

In order to easily compare the energy levels of the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center to those of the $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ center as obtained in x or γ irradiated crystals,[12] the fundamental level of U^{5+} and the charge-transfer level Γ_5 of U^{6+} at lower energy are represented on the same horizontal line. The energies given for U^{6+} are those of the Γ_5 levels which appear in all observed fine structures. We did not represent the center of gravity of the fine-structure lines since, as it will be shown in the following section, some fine-structure lines of several CTT's are not observed in the experimental spectra.

Figure 3(b) gives the energies of the levels Γ_5 at 19 869, 24 815, 26 570, 28 185, and 30 700 cm^{-1}, the energies of the levels Γ_1 at 19 286, 27 750, and 31 115 cm^{-1}, and the energy of the fluorescent Γ_2 level at 18 947 cm^{-1}. The band observed by Pustarov *et al.*[15] at 39 040 cm^{-1} has been added in Fig. 3(b).

This figure shows that seven energy levels at lower energy of the $5f^0$ configuration correctly coincide with the corresponding energy levels of the $5f^1$ configuration. More precisely, the energies, with respect to the energy of the Γ_5 level at 19 869 cm^{-1}, of the three lines at 24 815, 26 570, and 28 185 cm^{-1} differ by at most 500 cm^{-1} with respect to the energies of the lines at 4778, 6903, and 7848 cm^{-1} of the $5f^1$ configuration. The broad lines at 30 700 and 31 115 cm^{-1} can most likely be associated to the two lines at 11 939 and 12 030 cm^{-1} of the $5f^1$ configuration. The band observed by Pustarov *et al.*[15] at 39 040 cm^{-1} is shifted by ≈2800 cm^{-1} with respect to the line at 17 240 cm^{-1} of the $5f^1$ configuration.

The represented energy levels are those of the absorption

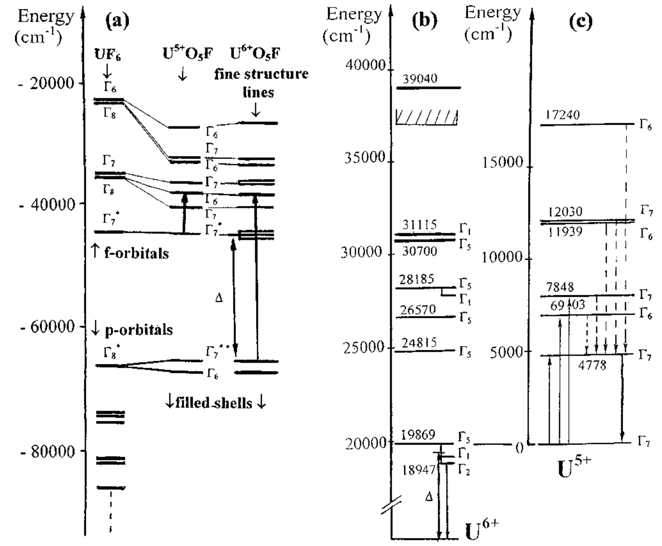

FIG. 3. (a) Monoelectronic energy levels of UF^6 as calculated by Onoe *et al.*[3] and schematic model for U^{6+} and U^{5+} transitions in UO_5F centers. The vertical scale gives the energies of the monoelectronic levels as given by Onoe *et al.* In (a), the filled *p* levels and empty *f* levels of UF^6 are represented on the left, the filled level at higher energy is denoted Γ_8^*, and the empty level at lower energy is denoted Γ_7^*. The experimental *f-f* transitions and *p-f* CTT's of U^{5+} and U^{6+} in UO_5F centers are also schematically represented. For U^{5+}, the Γ_7^{**} state is filled and one electron is on the Γ_7^* state. One *f-f* transition $\Gamma_7^* \leftrightarrow \Gamma_6$ is represented. For the $U^{6+}O_5F$ centers, the *p-f* CTT's are due to the transfer of one electron from the filled level Γ_7^{**} to the empty levels Γ_7^*, Γ_7, Γ_6, Γ_7, etc. at higher energy. One CTT from the fundamental level Γ_7^{**} to a fine-structure level $\Gamma_7^{**} \times \Gamma_6$ is shown. Δ is the energy difference between the center of gravity of the fine-structure lines of the first excited level and of the fundamental level $5f^0$. Δ can be considered as a measure of the "gap" between the filled *p* orbitals and the empty *f* orbitals. (a) also shows the splitting of the Γ_8 states of octahedral UF_6 into Γ_7 and Γ_6 states for the C_{4v} symmetry of UO_5F centers. The detailed experimental energy levels of $U^{6+}O_5F$ and $U^{5+}O_5F$ centers in LiF are given in (b) and (c). In order to conveniently compare the energies, the Γ_5 level of U^{6+} at 19 869 cm^{-1} is represented on the same horizontal line as the fundamental Γ_7 level of U^{5+}. The symmetry of the levels of U^{5+} is given to the right. The symmetry of the fine-structure lines is given for U^{6+}.

lines observed in the absorption spectra. If some absorption lines are phonon assisted lines, the represented energies have to be lowered by the energy $\hbar\omega$ of the relevant phonons in order to obtain the electronic levels. However, from the phonon assisted lines observed in the absorption spectra, we can estimate that $\hbar\omega$ is, at most, of 760 cm^{-1}.

IV. *f-f* AND *p-f* TRANSITIONS OF UO_5F CENTERS IN LiF

We will first determine the symmetry (Γ_6 or Γ_7 in C_{4v}^* symmetry) and the level ordering of the *f-f* transitions of U^{5+} in $U^{5+}O_5F$, and compare this level ordering to that obtained from relativistic molecular models for UF_6, UF_6^-, and NpF_6.

In the parametric model previously proposed to analyze the energy levels of the configuration $5f^1$ of $U^{5+}O_5F$ center in a crystal field of C_{4v} symmetry, the calculations are performed in the C_{4v}^* spinor group.[12] This model has permitted fitting the energies of the four Γ_7 states and the three Γ_6 states of the configuration $5f^1$ and the $g_\parallel$ and $g_\perp$ values of the fundamental level. For the fits reported in Ref. 12, the level ordering is, for increasing energy: Γ_7 (fundamental level), $\Gamma_7\,[\Gamma_8(3/2)]$, $\Gamma_6\,[\Gamma_8(1/2)]$, Γ_7, $\Gamma_6\,[\Gamma_8'(1/2)]$, $\Gamma_7\,[\Gamma_8'(3/2)]$, and Γ_6. The brackets indicate which doublet Γ_6 or Γ_7 is due to splittings of two quartets Γ_8 and Γ_8', which would be obtained in cubic O_h^* symmetry. Therefore, in cubic O_h^* symmetry, the level ordering for increasing energy would be Γ_7, Γ_8, Γ_7, Γ_8', and Γ_6 (see Fig. 3(a) for $U^{5+}O_5F$ centers).

It will now be shown that an overall description of the *p-f* and *f-f* transitions of U^{6+} and U^{5+} in LiF can be obtained by adapting the symmetry and the interpretations given for UF_6 and NpF_6 by Koelling *et al.*,[1] for UF_6 by Onoe *et al.*,[3] and for UF_6^- by Lewis *et al.*[2]

The relativistic Dirac-Slater scheme has been used in the molecular model developed by Koelling *et al.*[1] to determine the molecular orbitals of UF_6 and NpF_6 (and also PuF_6 for f^2 configurations). The molecular wave functions are constructed from the following *nlj* orbitals: $6p_{1/2}$, $6p_{3/2}$, $5f_{5/2}$, $5f_{7/2}$, $6d_{3/2}$, $6d_{5/2}$, and $7s_{1/2}$ for uranium and from the orbitals $2p_{1/2}$ and $2p_{3/2}$ for fluorine. The molecular energy levels are given in the spinor group O_h^* imposed by the relativistic model. The transitions, the associated electronic states, the nature (electric or magnetic dipole), and the energies are given by Koelling *et al.*[1] In the DS model of Onoe *et al.*[3] the orbitals $6s_{1/2}$ of uranium and $2s_{1/2}$ of fluorine have also been considered to determine the one electron energies of UF_6 [see Fig. 3(a)]. It must be noted that the level ordering in UF_6^{-2} and NpF_6[3] for *f-f* transitions is in agreement with that given by the parametric model, that is, for increasing energy: $4\Gamma_{7u}$, $13\Gamma_{8u}$, $5\Gamma_{7u}$, $14\Gamma_{8u}'$, and $11\Gamma_{6u}$. Furthermore, for UF_6, the relativistic molecular models predict that the occupied orbital at highest energy is $12\Gamma_{8u}$ [level Γ_8^* in Fig. 3(a) for UF_6].[1,3]

It will now be shown that seven empty *f* orbitals Γ_7 and Γ_6 and one filled *p* orbital Γ_7 [denoted Γ_7^{**} in Fig. 3(a)] intervene in the interpretation of the *p-f* transitions of $U^{6+}O_5F$ in LiF. The three lines Γ_2, Γ_1, and Γ_5, appearing at 18 947, 19 286, and 19 869 cm^{-1}, respectively, are fine-structure lines associated to *p-f* charge-transfer transitions from the filled *p* orbital Γ_7^{**} to the empty *f* orbital Γ_7^* at lower energy [see Fig. 3(a)]. More generally, in C_{4v} symmetry, orbitals $\Gamma_7 \times \Gamma_7$ or $\Gamma_6 \times \Gamma_6$ give fine-structure levels Γ_1, Γ_2, and Γ_5, while orbitals $\Gamma_7 \times \Gamma_6$ give only one allowed transition to a Γ_5 level and two forbidden transitions to levels Γ_3 and Γ_4. The corresponding transition of uranium in UF_6 is $12\Gamma_{8u} \rightarrow 4\Gamma_{7u}$ [levels Γ_8^* and Γ_7^* of UF_6 in Fig. 3(a)].

The lines at 24 815 cm^{-1} (Γ_5) and 26 570 cm^{-1} (Γ_5) are associated to *p-f* charge-transfer transitions from the filled *p* orbital Γ_7^{**} to empty *f* orbitals Γ_7 and Γ_6, respectively. For the line at 26 570 cm^{-1} the orbitals are $\Gamma_7 \times \Gamma_6$ and the fine-structure levels are Γ_3, Γ_4, and Γ_5, so that only one transition to level Γ_5 is observed since the other transitions are strictly forbidden in symmetry C_{4v}. We must note that one transition Γ_1 is lacking when associating the line at 24 815 cm^{-1} to orbitals $\Gamma_7 \times \Gamma_7$. In that case, three fine-structure levels Γ_1, Γ_2, and Γ_5 are expected, two electric dipole transitions to levels Γ_1 and Γ_5 should be observed and a magnetic dipole transition to the level Γ_2 should be very weak. The hypothesis that the filled *p* orbital is Γ_6 must be rejected since, in that case, other CTT's from the orbitals Γ_6 (filled), Γ_6 (empty) and Γ_6 (filled), Γ_7 (empty) should be observed. (In UF_6, the corresponding transition is $12\Gamma_{8u} \rightarrow 13\Gamma_{8u}$.)

The transitions at 27 750 cm^{-1} (Γ_1) and 28 185 cm^{-1} (Γ_5) are fine-structure lines associated to a *p-f* CTT from the filled *p* orbital Γ_7^{**} to the empty *f* orbital Γ_7, the associated fine-structure levels are Γ_1, Γ_2, and Γ_5. In that case, the very weak magnetic dipole transition to the level Γ_2 is not observed. (The corresponding transition in UF_6 is $12\Gamma_{8g} \rightarrow 5\Gamma_{7u}$.)

The line at 30 700 cm^{-1} of symmetry Γ_5 is a $\Gamma_7^{**} \times \Gamma_6'$ CTT. It corresponds to the level at 11 939 cm^{-1} of the configuration $5f^1$. This line corresponds to the transition $12\Gamma_{8u} \rightarrow 14\Gamma_{8u}$ of UF_6.

The broad line at 31 115 cm^{-1} of symmetry Γ_1 is a $\Gamma_7^{**} \times \Gamma_7$ CTT. However, this implies that one Γ_5 line is to be found in the broad line at 31 115 cm^{-1}. This line is to be associated to the level at 12 030 cm^{-1} of the configuration $5f^1$. This line corresponds to the transition $12\Gamma_{8u} \rightarrow 14\Gamma_{8u}$ of UF_6.

The broad band centered at 39 040 cm^{-1} can tentatively be considered as a $\Gamma_7^{**} \times \Gamma_6$ CTT [Fig. 3(a)]; in that case, the symmetry should be Γ_5. It is associated to the line at 17 240 cm^{-1} of the configuration $5f^1$. It corresponds to the transition $12\Gamma_{8u} \rightarrow 11\Gamma_{6u}$ of UF_6.

V. CONCLUSION

An analysis of well resolved absorption spectra in the near UV range and of previous polarized excitation and emission spectra of the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center in LiF has been made and the energy levels of this center have been compared with those of the $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ center. First, it has been shown that several well separated *p-f* CTT's of the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center can be obtained by translating the *f-f* transitions of the $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ center by ≈20 000 cm^{-1}. Second, the symmetry of several CTT's has been determined from (i) the symmetry of the levels of the $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ centers as previously given by a parametric model; (ii) the symmetry of the fine-structure lines of the CTT's; and (iii) a comparison with the structures of UF_6, UF_6^-, and NpF_6. Third, a coherent overall description of all observed energy levels has been proposed for the first time for both the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ and $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ centers in LiF.

When comparing the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ and $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ centers in LiF to UF_6 and UF_6^- molecules, several remarks can be made: (i) the CTT's of $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ as well as the *f-f* transitions observed in $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ cannot be simply accounted for by considering a weak *jj* coupling as in UF_6^-;[2] (ii) the vibronic structures are more simple for the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ center in LiF than for UF_6 molecules; and (iii) the energy levels of the $\mathrm{U}^{6+}\mathrm{O}_5\mathrm{F}$ and $\mathrm{U}^{5+}\mathrm{O}_5\mathrm{F}$ centers are well defined and separated thus facilitating the interpretation of the CTT's.

Finally, it must be noted that these molecular centers are unique in the sense that all energy levels of the configuration $5f^1$ of U^{5+} can be compared with seven energy levels of U^{6+} centers.

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