

## Anomalous Luminescence of Two $d^0$ Transition-Metal Complexes: $\text{KVOF}_4$ and $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$

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The luminescence properties at liquid helium temperature of the compounds  $\text{KVOF}_4$  and  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  are reported. Both compounds show vibrational structure in their emission spectra, the modes involved being a V-O stretching mode and a Nb-F bending mode, respectively. The decay times of the emission are uncommonly long compared to those of pure oxo  $d^0$ -complexes. It is shown that the forbidden nature of the lowest singlet-to-singlet transition is an important factor responsible for these long decay times. © 1992 Academic Press, Inc.

### Introduction

The optical properties of oxo  $d^0$  transition-metal complexes have been studied intensively for decades (1). Especially their luminescence properties have been the subject of many papers. This interest is not in the least based on the fact that these compounds can be applied in many ways, e.g., as lamp phosphors or as X-ray phosphors (1, 2).

The largest amount of work has been performed on tetrahedral and octahedral oxo complexes. There are, however, a few papers which report on the luminescence of  $d^0$  complexes with much lower symmetries than  $T_d$  or  $O_h$  (3-10). The luminescence properties of such systems are often quite different from those of the more symmetrical complexes, especially if one or more oxygens coordinating the metal ion are re-

placed by other ligands such as halogens (3, 8, 9). To gain more insight into the background of this different luminescence behavior, we started to investigate the luminescence of the compounds  $\text{KVOF}_4$  and  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ .

The crystal structure of  $\text{KVOF}_4$  has been described by Rieskamp and Mattes (11). It contains distorted  $\text{VOF}_5$  octahedra, linked by V-F-V bridges. However, one V-F distance in this bridge is much longer than the other, so that in first approximation there are isolated  $\text{VOF}_4$  entities present. The V-O distance of 1.57 Å is very short.

In the compound  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ , niobium has a  $4d^0$  configuration which compares with the  $3d^0$  configuration of vanadium in  $\text{KVOF}_4$ . The crystal structure is not precisely known. However, based on Raman and IR measurements (12), and also on the fact that the compound is isomorphous with  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$  (13), it has been established that  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  contains

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isolated  $\text{NbOF}_5$  octahedra. From the Raman and IR measurements it has also been shown that the Nb–O distance is very short (12). Possibly, the structure of the  $\text{NbOF}_5$  octahedron in the present compound is similar to that in the dehydrated compound of which the crystal structure has been reported (14). In  $\text{K}_2\text{NbOF}_5$  the Nb–O distance of 1.68 Å is also very short (14).

### Experimental

The starting materials used in the preparation procedures for the two compounds under investigation were  $\text{NH}_4\text{VO}_3$  (Merck, p.a.),  $\text{KHF}_2$  (Baker, p.a.),  $\text{Nb}_2\text{O}_5$  (Janssen, 99.99%), and hydrofluoric acid, 40% (Merck, p.a.)

$\text{KVOF}_4$  was prepared according to the procedure described in Ref. (11).  $\text{V}_2\text{O}_5$  was prepared from  $\text{NH}_4\text{VO}_3$  by thermal treatment at 600°C.  $\text{KHF}_2$  was used instead of  $\text{KF}$ . The phase purity was checked using X-ray powder diffraction. The compound is not very stable and turns from yellow to brown upon exposure to moist air.

$\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  was prepared and purified by recrystallization, according to procedures described in Ref. (13). The compound purity of the intermediate product  $\text{K}_2\text{NbF}_7$  was checked using X-ray diffraction (15). The X-ray pattern of the final product showed that it was a crystalline compound. No  $\text{K}_2\text{NbF}_7$  was found to be present in the final product.

Emission and excitation spectra were recorded down to 4.2 K using a Spex Fluorolog-2 spectrofluorometer, equipped with an Oxford flow cryostat. Decay measurements on  $\text{KVOF}_4$  were performed on a Molelectron nitrogen laser setup, described in detail in Ref. (16). Excitation was at 337 nm. The decay measurements on  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  were performed using a deuterium-filled Edinburgh Instruments 199F coaxial flashlamp. This setup is described in more detail in Ref. (17).

### Results

#### $\text{KVOF}_4$

At 4.2 K  $\text{KVOF}_4$  shows a rather intense photoluminescence. Figure 1 presents the excitation and emission spectra at 4.2 K. The excitation and emission maxima are at 365 and 710 nm, respectively. The Stokes shift amounts to  $13,500 \text{ cm}^{-1}$ . The full width at half maximum (FWHM) of the emission band amounts to about  $4000 \text{ cm}^{-1}$ . Above about 20 K the emission intensity starts to decrease. At about 140 K the intensity has dropped to 50% of its value at 4.2 K. The sharp feature in the emission spectrum at about 680 nm is probably due to a transition-metal impurity, such as possibly Cr or Mn.

The most interesting aspect of the luminescence spectra is the presence of vibrational structure in the emission band, which is observable below 140 K. On the average, the members of the progression are spaced at about  $990 \text{ cm}^{-1}$ . An origin is found at 500 nm. The sixth member of the progression is the one with the highest intensity.

Decay curves were measured from 2 to 200 K. At every temperature one-exponential curves were found. At low temperatures the decay time of 33.5 ms is very long. In Fig. 2, a graph of the decay time versus temperature is presented. Up to 50 K the decay time does not depend on the temperature.

#### $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$

The niobate also shows a rather intense photoluminescence at 4.2 K. The excitation and emission spectra at 4.2 K are presented in Fig. 3. The excitation and emission maxima are at about 250 and 450 nm, respectively. The Stokes shift amounts to about  $18,000 \text{ cm}^{-1}$ . The FWHM of the emission band amounts of  $5600 \text{ cm}^{-1}$  at 4.2 K. At higher temperatures the luminescence becomes weaker. At 120 K the emission intensity has decreased to 50% of its value at liquid helium temperature.

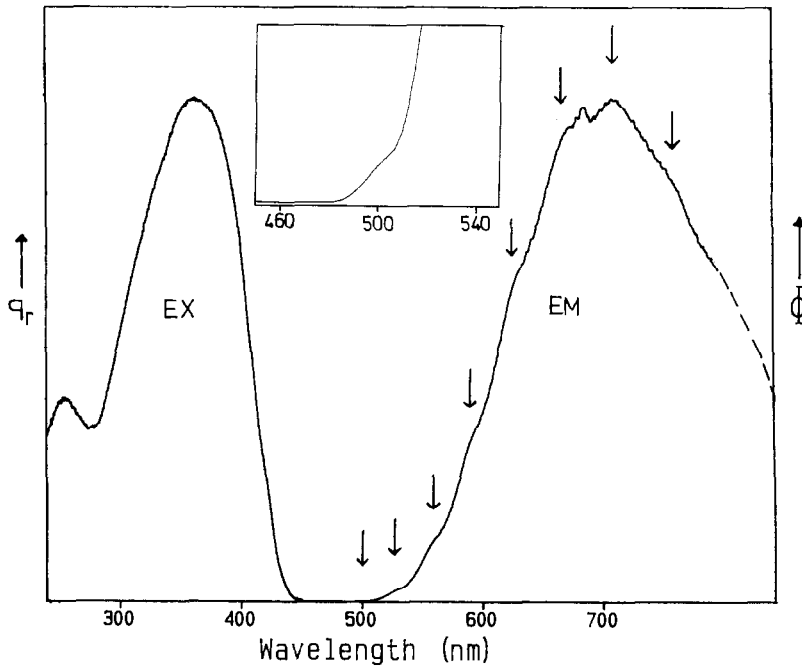


FIG. 1. Emission (EM) and excitation (EX) spectra of the luminescence of  $\text{KVOF}_4$  at 4.2 K. The arrows indicate the positions of the consecutive members of the vibrational progression.  $q_r$  gives the relative quantum output and  $\phi$  the radiant power per constant wavelength interval, both in arbitrary units. The inset presents a magnification of the emission spectrum around 500 nm.

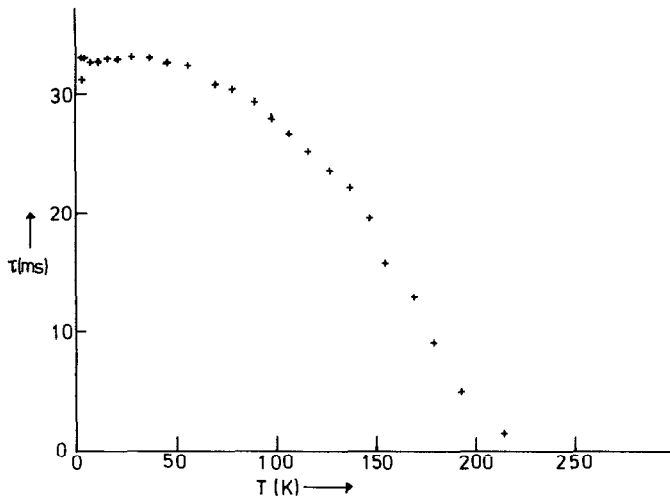


FIG. 2. Temperature dependence of the decay time of the emission of  $\text{KVOF}_4$ . Excitation is at 337 nm.

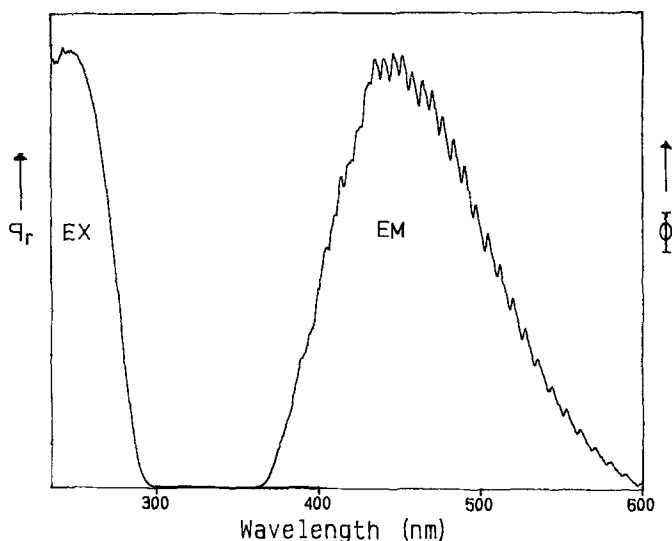


FIG. 3. Emission (EM) and excitation (EX) spectra of the luminescence of  $K_2NbOF_5 \cdot H_2O$  at 4.2 K.

As in the case of  $KVOF_4$ , vibrational structure is observed on the emission band. The frequency of the vibrational mode involved is, however, different. The members of the progression are on the average spaced at  $290\text{ cm}^{-1}$ . It is not possible to determine which member has the highest intensity, since the vibrational structure is not very well resolved on the short wavelength side of the emission band.

Decay curves were measured from 4.2 to 100 K and were found to be exponential. At 4.2 K the decay time amounts to  $560\ \mu\text{s}$ . At higher temperatures the decay time becomes longer. At 70 K the decay time amounts to  $680\ \mu\text{s}$ . A graph of the decay time versus temperature is presented in Fig. 4.

## Discussion

### $KVOF_4$

The excitation and emission bands are, as usual for pentavalent vanadium, ascribed to charge-transfer transitions (1, 18). The electronegativity of fluorine is larger than that

of oxygen. Therefore, the electronic transitions are expected to involve the excitation of an electron from a molecular orbital (MO) having predominant oxygen  $2p$ -character, to a MO having predominant vanadium  $3d$ -character (3, 18).

In the IR spectrum of this compound there is a strong absorption at  $1020\text{ cm}^{-1}$ , which is ascribed to the V–O stretching vibration (11). This value is in rather good agreement with the average energy difference between the members of the vibrational progression in the emission spectrum. The assumed localization (see above) of the excited state in the V–O bond is in this way confirmed by the observation of a progression in the V–O stretching mode.

The appearance of vibrational structure in the emission spectra of vanadates and other oxo  $d^0$ -complexes, is very uncommon (1, 18). It has been shown that for oxo tetrahedral vanadates the emissive state couples with several Jahn–Teller active deformation vibrations, in addition to the generally assumed coupling with the totally symmetrical stretching mode (19, 20). This is most proba-

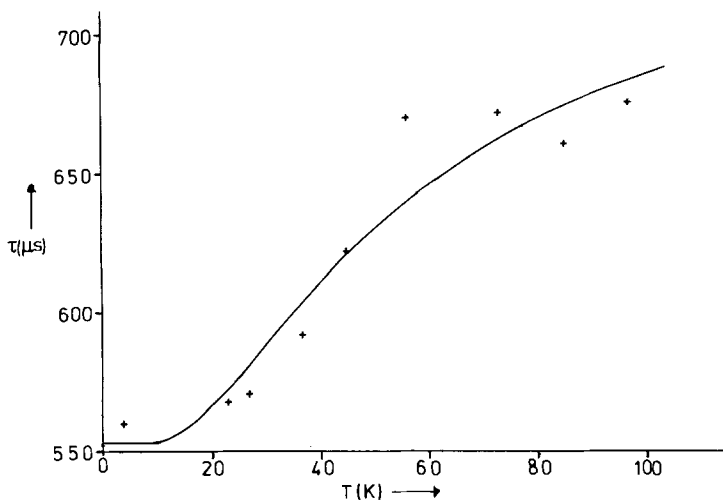


FIG. 4. Temperature dependence of the decay time of the emission of  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ . The solid line represents a fitted curve, see text.

bly the reason why no structure is observed in the emission spectra of these latter compounds, because coupling with several vibrations smears out all of the vibrational structure. The observation of vibrational structure in the present case is ascribed to the fact that the excitation is more or less localized in the diatomic V–O entity. Such a linear entity has only one vibrational mode.

The FWHM of the emission band and the Stokes shift are similar to values found for tetrahedral oxo vanadates (18).

The decay time of 33.5 ms at low temperatures is very long. It has been shown that the emitting level in the case of metal  $d^0$ -complexes has a triplet character, whereas the ground state has singlet character (19–21). However, the present decay time is an order of magnitude longer than usually observed for tetrahedral oxo vanadates, for which decay times have been observed of about 1 ms (18). The spin selection rule seems, therefore, not to be sufficient to account for this very long decay time.

In a simple picture, the energy level scheme of a  $d^0$  complex consists of low-lying excited triplet levels and higher-lying

excited singlet levels (1, 21). The triplet-to-singlet emission transition can “steal” intensity from a singlet-to-singlet transition of suitable symmetry by spin-orbit coupling (21). The most important parameters which determine the decay time of the emission of a  $d^0$  complex are therefore: (1) the oscillator strength of the relevant singlet-to-singlet transition, (2) the energy difference between the relevant excited triplet and singlet states, and (3) the value of the matrix element  $\langle \Phi(T) | H(\text{s.o.}) | \Phi(S) \rangle$ , determining the spin-orbit coupling.

With respect to point (1), the oscillator strengths of these singlet-to-singlet transitions can be determined from absorption spectra of aqueous solutions of the relevant  $d^0$  complexes. In these spectra the spin-forbidden singlet-to-triplet transitions are not observed (1). The  $\text{VOF}_4^-$  anion is stable in 40% hydrofluoric acid solutions and has in solution about the same structure as in  $\text{KVOF}_4$  (22). The  $\text{VO}_4^{3-}$  anion is stable in strongly basic solutions (23).

Figures 5a and 5b present the absorption spectra of a solution containing  $5 \times 10^{-4}$  moles vanadium per liter in 40% hydroflu-

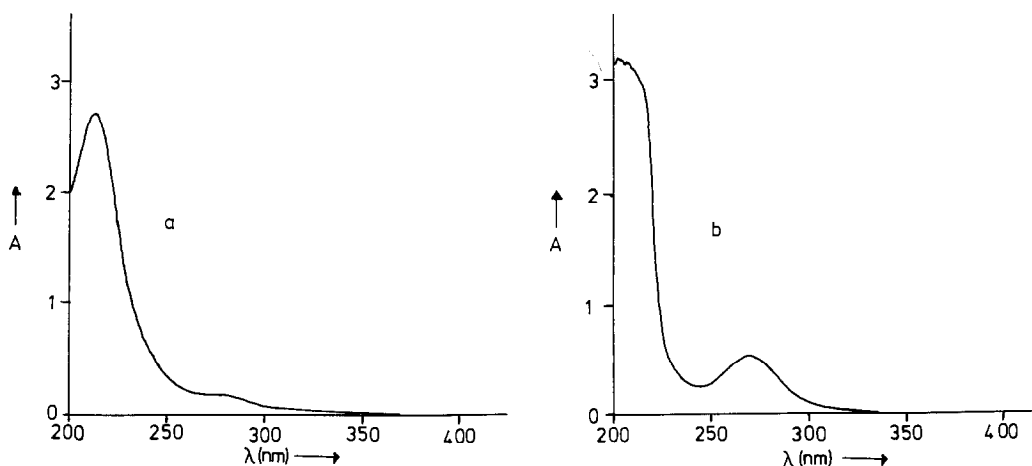


FIG. 5. Absorption spectra at room temperature of (a) a  $2.5 \times 10^{-4} M$  solution of  $V_2O_5$  in 40% HF; (b) a  $10^{-4} M$  solution of  $NH_4VO_3$  in 2M KOH in water. "A" denotes the absorbance. Note that the vanadium concentration for Fig. 5a is five times higher than for Fig. 5b.

oric acid and of a solution containing  $1 \times 10^{-4}$  moles vanadium per liter in 2M KOH, respectively. Note that the concentrations of the active species are different in the two absorption spectra.

The spectrum in Fig. 5b is similar to the one reported in Ref. (23), insofar that the absorbance of the band at 210 nm is much higher in the present case compared to Ref. (23). The absorbance of this band is probably not very reliable due to the weakness of the lamp of our spectrophotometer in this spectral region. In Ref. (23) the oscillator strengths of the transitions at 210 and 270 nm are reported to amount to 0.12 and 0.15, respectively. In Fig. 5a there are bands observed at 215 and 280 nm. The tail of this latter band toward longer wavelengths might be a separate band. From this spectrum the oscillator strength of the transition at 280 nm is estimated to amount to  $6 \times 10^{-3}$ . As argued above, we do not think that the absorbance of the band at 215 nm is very reliable.

The decay time of the triplet-to-singlet emission is inversely proportional to the oscillator strength of the relevant singlet-to-

singlet absorption transition from which the intensity is stolen (21). The oscillator strength of the singlet-to-singlet transition of the  $VOF_4^-$  complex at 280 nm is an order of magnitude smaller than those in the case of the  $VO_4^{3-}$  complex. This suggests strongly that the 280 nm transition is involved in the spin-orbit coupling and that its low oscillator strength is at least one of the factors responsible for the long decay time of the  $VOF_4^-$  complex.

For  $KVOF_4$  the decay time does not depend on the temperature from 2 to 50 K. This may indicate that there are no other higher-lying triplet levels present within about  $30 \text{ cm}^{-1}$  from the lowest emitting triplet level (1). However, if such levels are present anyhow, they must decay with the same time constant as the lowest triplet level. This temperature dependence of the decay time is different from what is usually observed for tetrahedral oxo vanadates. Below 30 K, the decay for these compounds often shows a relatively strong decrease or increase with temperature (18).

The decrease of the decay time with temperature above 50 K is due to nonradiative

transitions (the luminescence intensity decreases also in this temperature region) or to thermal occupation of radiative singlet levels (24).

As we have shown above, the luminescence properties of  $\text{KVOF}_4$  are quite different from those of oxo tetrahedral vanadates. There is, however, one system which has luminescence properties which are very similar to those of  $\text{KVOF}_4$ , namely silica supported vanadium catalysts. This catalyst also shows a vibrational progression on its emission band in a vibration that has a frequency of  $1040 \text{ cm}^{-1}$  at low temperatures (25). The decay time of the emission of this catalyst at 4.2 K amounts to 35 ms (26).

The luminescence of this catalyst is usually ascribed to monomeric  $\text{VO}_4$  entities, in which vanadium is in the pentavalent state. Three oxygens of the entity are directly bonded to the silica surface, and the fourth oxygen is bonded to the other side of the vanadium ion with a very short bond (25). The structural similarity of this luminescent center with the  $\text{VOF}_4^-$  unit in  $\text{KVOF}_4$  is clear.

From this latter comparison it seems that the low oscillator strength of the lowest singlet-to-singlet transition (and subsequently the long decay time) is associated with the presence of a very short V–O bond. As a matter of fact, the same relation between the decay time and the presence of a short metal-to-oxygen bond has been observed before for some titanates (6) and, as is discussed below, some niobates. An explanation for the low value of the oscillator strength is obviously hidden in the nature of the orbitals involved in the optical transitions in such complexes. Ab initio calculations will possibly clarify this nature.

#### $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$

As for all niobates the optical transitions in  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  are of the charge-transfer type. The positions of the excitation and emission maxima are not uncommon for iso-

lated niobate octahedra (27, 28). Although the excitation maximum is at a high energy, the quenching temperature is low compared to oxo niobates which have their excitation maximum at about the same energy (27, 29). It has been shown that the quenching temperature of oxo niobates increases when the absorption edge shifts to higher energies (27, 29).

The appearance of vibrational structure in the emission bands of niobates is, just as for vanadates, unusual. The excited state in the case of  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  couples with a different vibrational mode than observed for  $\text{KVOF}_4$ . The vibration, which has a frequency of  $290 \text{ cm}^{-1}$ , is ascribed to a Nb–F bending mode (30). It cannot be excluded that coupling with the Nb–O stretching vibration ( $\nu = 935 \text{ cm}^{-1}$  (12)) occurs also, but that the structure in the emission band due to this coupling is not well resolved. From Fig. 1 it is clear that in the case of  $\text{KVOF}_4$  the vibrational structure is also not extremely well resolved.

In the Raman spectrum of this compound a line is observed at  $295 \text{ cm}^{-1}$  (12). A unique assignment of this Raman line is, however, not made in this latter paper. Since the Raman spectra of  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  and  $\text{CsNbF}_6$  show some similarities, it is suggested by the author of that paper that the  $295 \text{ cm}^{-1}$  line is due to a vibration which resembles the  $\nu_5$  ( $T_{2g}$ ) mode of a regular octahedron (12).

However, recently the luminescence of the compound  $\text{K}_2\text{NaTiOF}_5$  has been reported (3). In the crystal structure of this compound there are isolated  $\text{TiOF}_5$  octahedra (3). Titanate luminescence is of the same type as niobate luminescence. For this titanate compound there is also a progression observed in the emission band, in a vibration which has a frequency of  $290 \text{ cm}^{-1}$ . In this case this vibration was ascribed to a  $\gamma(\text{Me}-\text{F}_4)$  mode (3).

Nevertheless, it was expected for  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  that only coupling with the

Nb–O stretching vibration would occur, since the structures of the luminescent centers in  $\text{KVOF}_4$  and  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  are very similar. The reason for this different behavior is not clear. It is to be expected that it is related to the different nature of the molecular orbitals which are involved in the optical transitions.

The decay time of  $560 \mu\text{s}$  at 4.2 K is shorter than the one found for  $\text{KVOF}_4$ . This is, as usual, ascribed to the stronger spin–orbit coupling, which relaxes the spin selection rule in the case of heavier nuclei (1, 21). This decay time is longer than found for isolated oxo niobate octahedra, in which case decay times of about  $100 \mu\text{s}$  have been observed (28). It is clear that the observation of such a relatively long decay time resembles the result for  $\text{KVOF}_4$ .

A similarly long decay time of  $500 \mu\text{s}$  was reported recently for  $\text{CsNbO}(\text{P}_2\text{O}_7)$  at 4.2 K (5). This is not surprising considering the crystal structure of this compound. It contains isolated distorted  $\text{NbO}_6$  octahedra, one oxygen of which is bonded with a very short bond to the niobium ion (5). The similarity with the structure of  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  is clear.

In contrast with  $\text{KVOF}_4$ , the decay time changes with temperature in the low temperature region. Since the decay time becomes longer, the change cannot be due to nonradiative decay. If the approximation is made that emission takes place from two excited triplet levels, one of which is thermally occupied at higher temperatures, the data in Fig. 4 can be fitted to a three level scheme as described in Ref. (31). It is assumed that there is thermal equilibrium between the excited levels (31). The solid line in Fig. 4 represents this fit. From the fit, the energy difference between the excited levels is found to amount to  $40 \text{ cm}^{-1}$ . The decay times are  $550$  and  $1,300 \mu\text{s}$  for the lower and the higher emitting level, respectively.

The luminescence properties of  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  are very similar to those reported

some time ago for  $\text{K}_2\text{NbF}_7$  (32). This suggests that the luminescence reported in that paper is due to  $\text{NbOF}_5$  entities in the samples, which are expected to be formed by incorporation of minor amounts of oxygen or water into the lattice of  $\text{K}_2\text{NbF}_7$ . The replacement of two fluorines by one oxygen can be achieved without charge compensation. As a matter of fact, we investigated the luminescence properties of freshly prepared  $\text{K}_2\text{NbF}_7$ , and we did observe at 4.2 K an emission band at 480 nm without any vibrational structure.

In conclusion, we have reported the luminescence of  $\text{KVOF}_4$  and  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ . Both compounds show vibrational structure in their emission spectra which is very unusual for  $d^0$  transition-metal complexes. The vibrational mode which couples with the electronic excited state is different for the two compounds. The decay times of the emission of both compounds are long. This is ascribed to the forbidden nature of the singlet-to-singlet transition, from which the emission transition "steals" its intensity. Ab initio calculations are necessary to clarify the nature of the orbitals involved in the optical transitions. This may lead to an explanation of the long decay times.

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