ION-ION INTERACTION AND ENERGY TRANSFER OF
4+ TRANSURANIUM IONS IN CERIUM TETRAFLUORIDE

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Abstract

Dynamics of excited 5f electron states of the transuranium ions Cm^{4+} and Bk^{4+} in CeF_4
are compared. Based on time- and wavelength-resolved laser-induced fluorescence, excitation
energy transfer processes have been probed. Depending on concentration and electronic energy
level structure of the studied 4+ transuranium ion, the dominant energy transfer mechanisms
were identified as cross relaxation, exciton-exciton annihilation, and trapping. Energy transfer
rates derived from the fitting of the observed fluorescence decays to theoretical models, based on
electric multipolar ion-ion interactions, are contrasted with prior studies of 4f states of 3+
lanthanide and 3d states of transition metal ions.

DISCLAIMER

Introduction

Most spectroscopic studies of actinide (5f) ions have focused on determination of electronic energy level structure. The dynamic nature of 5f states is largely unexplored. Based on the greater radial extent of 5f electron wave functions, with respect to those of the shielding 6s and 6p shells, the mobility of excited 5f states of actinide ions in compounds is expected to be intermediate between that of excited 4f states of lanthanide ions and 3d states of transition-metal ions [1,2]. Time- and frequency-resolved fluorescence decay technique provides a powerful probe for the excited-state dynamics and energy transfer arising from ion-ion interactions in solids. A previous fluorescence-line-narrowing study on Np^{3+} in $LaCl_3$ found large electron-phonon interaction [3], and a recent fluorescence study provided evidence of energy transfer between U^{4+} ions in different sites in U^{4+}:$ThBr_4$ compound [4].

With tetravalent actinides doped into CeF_4, we are carrying out systematic spectroscopic studies of electronic state energy level structure as well as determining the dynamical properties of excited 5f states. Our recent results from studies on Cm^{4+} and Bk^{4+} have shown that the spectra and dynamics of the 4+ actinide ions can be quite complicated due to ion-ion and ion-lattice interactions and due to the comparatively dense 5f state structure of transuranium 4+ ions.

Energy Transfer Mechanisms

Among all energy transfer processes, cross relaxation and up conversion are of particular significance because they influence the fluorescence yield and quantum efficiency of optical systems and are ideal for time- and frequency-resolved study of excited-state dynamics. In the presence of large number of defects or impurities, trapping is an important energy transfer mechanism and can dramatically quench intrinsic fluorescence.

1. Cross Relaxation and Trapping

Cross relaxation is a self trapping process in which donors act as their own acceptors.([8-10](#)) In cross relaxation, an excited ion interacts with and gives up a part of its excitation energy to a neighboring ion in a lower state. The net result is that both ions end up in one or two different intermediate energy states, thereby quenching the fluorescence from the originally excited state. In resonant cross relaxation, the sum of the energies of the intermediate states is equal to the initial excitation energy. In the non-resonant case, energy conservation is achieved via creation or destruction of phonons. The well-known Inokuti-Hirayama irreversible energy transfer model ([11](#)) is often used to interpret the experimental observation of nonexponential fluorescence decays due to irreversible energy transfer processes, such as cross relaxation and trapping. At low actinide ion concentration, an integration approximation, instead of a lattice ensemble average, is appropriate and, $n(t)$, the excited ion density at time t is given by([5-7](#))

$$n(t) = n(0)\exp[-k_0 t - C_t \Gamma(1-3/s)(W_t t)^{3/s}], \tag{1}$$

where $n(0)$ is the initial excited ion density, k_0 is the reciprocal lifetime of the excited state, $C_t=(4\pi/3)R_0^3 n_t$ with R_0 and n_t representing the nearest neighbor separation and acceptor density, respectively, and $\Gamma(1-3/s)$ is the gamma function. The parameter W_t is the cross-relaxation rate or trapping rate for nearest neighbors. The value of s is 6, 8, or 10 for electric dipole-dipole, dipole-quadrupole, or quadrupole-quadrupole interaction, respectively.

2. Up Conversion

Up conversion via exciton-exciton annihilation is a special type of cross-relaxation process in which two identical ions, both initially in the excited state, interact ([9-12](#)). The result is promotion of one ion to a higher excited state via loss of energy from the other ion. Any energy mismatch is accommodated via creation or destruction of phonons. Since this

annihilation process simultaneously quenches both initially excited ions, it results in a second order decay (12,13). If the exciton-exciton annihilation is the only energy transfer mechanism, and all excited ions have identical excitation probability as in Eq. (1), one can derive the decay of the excited ion density in the presence of exciton-exciton annihilation as (3,11)

$$n(t) = \frac{n(0)k_0}{(k_0 + C_e W_a)\exp(k_0 t) - C_e W_a}, \qquad (2)$$

where $n(0)$ is the initial excited ions per unit volume, $C_e = 4\pi R_0^3 n(0)/(s-3)$, and W_a is the annihilation rate for nearest neighbors.

For a given system, there can be more than one energy transfer mechanisms involved. Particularly, in the presence of both up conversion and cross relaxation or trapping, fluorescence decay becomes complicated and separation of the involved energy transfer mechanisms is not always trivial. In this case, nonexponential fluorescence decays are not describable by the Inokuti-Hirayama or exciton annihilation models, and incorporation of different energy transfer models is necessary to describe the fluorescence dynamics. Based on the Forster-Dexter energy transfer theory, we have developed a new model to account for the transfer probabilities of exciton-exciton annihilation and the site-dependent trapping process (16). With the assumption of electric dipole-dipole interaction and the integration approximation, the derived decay of the excited-ion density is

$$n(t) = \frac{n(0)(k_0 + C_t W_t)}{(k_0 + C_t W_t + C_e W_a)\exp[k_0 t + C_t(\pi W_t t)^{1/2}] - C_e W_a}, \qquad (3)$$

where all parameters are same as defined in Eq. (1) and Eq. (2).

Experimental

A tunable dye laser pumped by a Q-switched Nd:YAG laser was used as the excitation source. Fluorescence from the sample contained in a variable temperature cryostat was selected using long pass filters, dispersed with a 1 meter monochromator, and detected using a cooled photomultipliers (GaAs and S-1 photocathodes). Fluorescence dynamics were measured using a transient recorder (LeCroy TR8818) connected to a DEC 11/23+ minicomputer which carried out add-to-memory signal averaging of the transient recorder data. Such signal averaging was carried out over a few to as many as 2048 laser pulses. The input resistance of a buffer amplifier connected to the photomultiplier was varied to provide a range of system response times. The data were transferred to a local area VAX cluster where a non-linear least squares fitting procedure was used to analyze the observed fluorescence decays according to the energy transfer models.

Selective laser excitation was utilized to unravel the complex multisite spectra of $An^{4+}:CeF_4$ and to probe the dynamics of the excited f-states of the actinide ions on the nonequivalent sites. Details of site symmetry and selective excitation are given in Refs. 5 and 14.

Results and Discussion

1. $Cm^{4+}:CeF_4$

Fluorescence decay measurements and quantitative analysis have been carried out on the selected actinide ion Cm^{4+} in host material CeF_4 (5). The actinide ion Cm^{4+} has a J=0 singlet ground state ($^7F_0$) and, when substituted for Ce^{4+}, can occupy either of the two crystallographic metal ion sites in CeF_4. The lowest component of the second J=1 multiplet was the only emitting metastable state found in this system, and all fluorescence dynamics studies were

carried out on this state.([5](#)) The energy of the emitting metastable state is 19916 cm^{-1} for Cm^{4+} on one of the two distinct ion sites, arbitrarily termed site A, and 19911 cm^{-1} for Cm^{4+} on the other ion site, termed site B.

Fluorescence decay studies have been carried out on two samples, one of 0.1 atom% Cm^{4+} concentration and the other of 5 atom% Cm^{4+} concentration ([5](#)). Nonexponential fluorescence decays of Cm^{4+} were observed in both samples at all laser power and from 4 to 300 K. In the 0.1 atom% Cm^{4+} sample, cross relaxation was identified as the predominant energy transfer process. From the observed fluorescence spectra, energy levels of the lowest-lying J=3 and J=4 multiplets are the intermediate states for resonant cross relaxation. When Cm^{4+} ion on either site is excited, there are more than six channels providing cross relaxation with energy mismatches from 0 to 20 cm^{-1}. Additional combinations of vibronic components of the J=0,5,6 states lying below the emitting level and the electronic levels of the first J=1,2 multiplets may also be involved in cross relaxation. In electric dipole-dipole interaction, according to Eq. (2), the resonant cross relaxation rate is proportional to corresponding optical transition probability. The observed emission and absorption spectra provided evidence that cross relaxation may be much more efficient than resonant donor-donor transfer because the optical transition probabilities from the emitting state and the ground state to these intermediate states are about three orders of magnitude higher than that of the transition between the ground state and the emitting state.

As described above, the large number of cross-relaxation pathways with small energy mismatches and the relatively high transition probabilities account for the efficient cross relaxation that causes the observed nonexponential fluorescence decays. The decays observed at low excitation intensity in the 0.1 atom% Cm^{4+} sample have been well fit ([5](#)) by Eq. (1) with the approximation of electric dipole-dipole interaction (s=6). The derived decay parameters k_0 and W_t are given in Table I. Figure 1(a) shows the decay data and the fit of the 16584 cm^{-1}

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fluorescence of the site B Cm^{4+} ions from the emitting state to the lowest state of the lowest-lying J=1 multiplet.

As evidenced by the substantially higher fluorescence quenching found in the 5 atom% Cm^{4+} sample, the observed energy transfer rate increased with increasing Cm^{4+} ion concentration . In the 5 atom% sample, the decay rate at long times was same as that for 0.1 atom% sample, but the initial decay rate increased with the excitation intensity. Equivalently, at the fixed excitation intensity, the initial decay rate exciting at the absorption line center was higher than when exciting in the wings of the line. These observations suggest that exciton-exciton annihilation dominants the observed excited-state dynamics in 5 atom% sample although trapping and cross relaxation may also be stronger than in the 0.1 atom% sample. The large transition probabilities from the fluorescent level to higher-lying states in the range from 30000 cm^{-1} to 40000 cm^{-1}, evidenced by efficient two-photon excitation, also indicated that up conversion must be taken into account. Moreover, broad band emission from Cm^{4+} ions on trap sites was observed. Since the trap emission overlapped the intrinsic fluorescence, the observed fluorescence decays of Cm^{4+} in the 5 atom% sample became more complicated than in the 0.1 atom% sample where trapping was negligible. Equation (3) has been use to fit the nonexponential decays of the fluorescence from the 5 atom% Cm^{4+} sample. The fit values of parameters are list in Table I. Figure 1(b) shows the fluorescence decay data of Cm^{4+} in the 5 atom% sample. The solid curve is a fit to Equation (3), the exciton-exciton annihilation model incorporating trapping and cross relaxation (5). The fluorescence was induced and monitored in the same way as for the data shown in Figure 1(a).

2. Bk^{4+}:CeF_4

The Bk^{4+}:CeF_4 sample studied was one in which two Bk^{4+} fluorescing states, one at 16375 cm^{-1} and the other at 20360 cm^{-1}, previously had been observed in emission terminating on components of the $^8S_{7/2}$ ground state (15). The 16375 cm^{-1} emitting state corresponds to the

lowest energy component of the first exited J=7/2 multiplet while the 20360 cm^{-1} state is the lowest energy component of the first excited J=5/2 multiplet.([15]) The $^{249}Bk^{4+}$:CeF$_4$ sample, when originally prepared, contained 1 atom% Bk (i.e., Bk$_{0.01}$Ce$_{0.99}$F$_4$), but, due to beta decay of ^{249}Bk, the Bk content was 0.05 atom% at the time of the present work (with 0.95 atom% of decay daughter ^{249}Cf). Following excitation at 28195 cm^{-1}, the observed decay of the Bk^{4+} emitting state at 20360 cm^{-1} was predominantly exponential with a lifetime of 0.7 μs. The exponential character of the decay of 20360 cm^{-1} state provides evidence that radiative emission of photons and nonradiative emission of phonons are the predominate deexcitation processes influencing its dynamics. In contrast, the decay of 16375 cm^{-1} state was always nonexponential at short times following pulsed (5 ns) laser excitation. At long times, the decay of the 16375 cm^{-1} state was found to be exponential with a lifetime of 550 μs.

Emission from the 20360 cm^{-1} state was also observed when the laser wavelength was tuned from 16375 to 17775 cm^{-1} to pump Bk^{4+} ions into the components of the first excited (J=7/2) multiplet. This emission from the 20360 cm^{-1} state, termed anti-Stokes fluorescence, exhibited very different dynamics than that observed from the same emitting state when using 28195 cm^{-1} excitation. The time evolution of the anti-Stokes fluorescence exhibited a fast initial decay followed by a nonexponential slower decay on a longer time scale. The dominant fast initial decay appears exponential with a decay time of circa 0.7 μs, similar to that observed following excitation at 28195 cm^{-1}.

A number of processes can lead to the observed anti-Stokes fluorescence: (a) step-wise excitation and direct two-photon absorption,([5]) (b) up-conversion due to energy transfer among the excited Bk^{4+} ions,([8-10]) and (c) cooperative emission or up-conversion of coupled ion pairs ([9,10]). Process (c) can be ruled out because of the lack of additional spectral lines due to ion pairs. Only process (b) provides a rationale for the observed long time nonexponential decay of the 20360 cm^{-1} state following excitation of Bk^{4+} bands in the range from 16375 to 17775 cm^{-1}. An up-conversion process involving the long-lived 16375 cm^{-1} state evidently feeds the 20360 cm^{-1} state, resulting in anti-Stokes fluorescence whose dynamics thereby becomes

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coupled to that of the 16375 cm^{-1} state. We attribute the observed anti-Stokes emission from the 20360 cm^{-1} state to contributions from processes (a) and (b), i.e. two-photon excitation followed by rapid nonradiative decay to the 20360 cm^{-1} state and energy transfer involving the 16375 cm^{-1} state of Bk^{4+} that results in up-conversion over a much longer time scale.

The importance of up-conversion processes in this system has also been confirmed by observation of excitation-intensity dependent Stokes fluorescence decays using 17775 cm^{-1} excitation. The initial decay rate of the 16375 cm^{-1} state is higher using 28 MW/cm^2 excitation intensity than at 1 MW/cm^2 excitation intensity, an intensity at which anti-Stokes fluorescence was not observable. These observations provide evidence for an excitation-excitation annihilation process that quenches Stokes fluorescence at short times. When the excitation intensity was reduced low enough (such as 1 MW/cm^2) that anti-Stokes fluorescence was no longer observable, the fluorescence decay of the 16375 cm^{-1} state was still nonexponential. This provides evidence that, in addition to up-conversion, energy transfer occurs through other channels such as trapping and cross relaxation in which the acceptor is initially in its ground state. In this system, cross relaxation can be ruled out because of the lack of intermediate energy levels. In addition to the Bk^{4+} ions on different sites, Cf^{4+} impurity ions, whose excitation energy bands overlap the 16375 cm^{-1} emitting state of Bk^{4+}, have been shown to act as traps. Delayed fluorescence from Cf^{4+} at 11543 cm^{-1} was found after excitation of the 17775 cm^{-1} state of Bk^{4+} (16). At low excitation intensity, up conversion was negligible and the fluorescence decays were fit very well by the trapping model [Eq. (1) or set $C_e = 0$ in Eq. (3)]. At high excitation intensity, it was necessary to use Eq. (3) to fit the Bk^{4+} fluorescence decays, indicating the presence of both up conversion and trapping.

For Cm^{4+} and Bk^{4+}, fit values of decay parameters, and their estimated errors based on nonlinear least squares analysis, are listed in Table I. The fit values of k_0 and W_t are independent of the excitation intensity. The value of W_a for Bk^{4+} is based on fitting the high excitation intensity (28 MW/cm^2) induced fluorescence data shown in Figure 1(c) (13657 cm^{-1}

fluorescence monitored following 17775 cm^{-1} excitation). No value for W_a was determined for 0.1 atom% Cm^{4+} because its observed decay was independant of laser excitation intensity.

Table I. Fluorescence decay parameters of Cm^{4+} and Bk^{4+} in CeF_4 at 4 K

Ion	Concentration (atom%)	k_0 (s^{-1})	W_t (s^{-1})	W_a (s^{-1})
Cm^{4+}	0.1	$(3.8\pm0.019)X10^3$	$(1.2\pm0.005)X10^8$	not applicable
Cm^{4+}	5	$(4.0\pm0.12)X10^3$	$(3.2\pm0.13)X10^{8\cdot}$	$(2.0\pm0.2)X10^8$
Bk^{4+}	0.05	$(1.85\pm0.009)X10^3$	$(3.2\pm0.03)X10^7$	$(6.0\pm0.4)X10^9$

Parameters W_t and W_a in Table I provide a direct measure of energy transfer rate which reflects the strength of ion-ion interaction at a given distance. It is noted that the value of W_t for Cm^{4+} is about one order of magnitude lager than that for Bk^{4+}. This is attributed, as indicated earlier in this paper, to resonant cross relaxation of the excited states of Cm^{4+} and the absence of this decay channel in case of the emitting state of Bk^{4+}. For Bk^{4+} in CeF_4, W_t primarily represents the transfer rate arising from energy transfer to Cf^{4+} ions acting as trap sites. The W_a values shown in Table I result from fits in which the value of C_e was fixed (C_e is proportional to the initial excited ion density). Due to uncertainties in the absorption cross-section and laser fluence, we estimate that the value of C_e used may be in error by as much as a factor of 5 which introduces a corresponding large uncertainty in the absolute value of W_a. Nevertheless, we have extracted a useful estimate of the contribution of the exciton-exciton annihilation in the presence of other energy transfer processes. The derived annihilation coefficients, defined as $(4\pi/3)R_0^3W_a$, of Cm^{4+} and Bk^{4+} are of order $2X10^{-14}$ and $1X10^{-13}$ cm^3s^{-1}, respectively. As might be expected for 5f excited states, this value lies between that the value of $5X10^{-15}$ cm^3s^{-1}

reported for 4f states of a rare-earth ion ([12]) and that of 5×10^{-13} $cm^3 s^{-1}$ reported for 3d states of transition-metal ions ([13]).

Concluding Remarks

Our work is providing the first fundamental insight into the dynamics and energy transfer mechanisms of 5f electronic states of 4+ actinide ions. The large energy transfer rates found for 5f states of Cm^{4+} and Bk^{4+}, in comparison with 4f states of 3+ lanthanide ions, are attributed to the extended character of 5f electron orbitals and resultant strong ion-ion interaction in comparison with 4f electron orbitals. Dense 5f state energy level structure, in the range from 30000 cm^{-1} to 40000 cm^{-1}, plays an important role in the up-conversion processes observed in our Cm^{4+} and Bk^{4+} studies.

Acknowledgements

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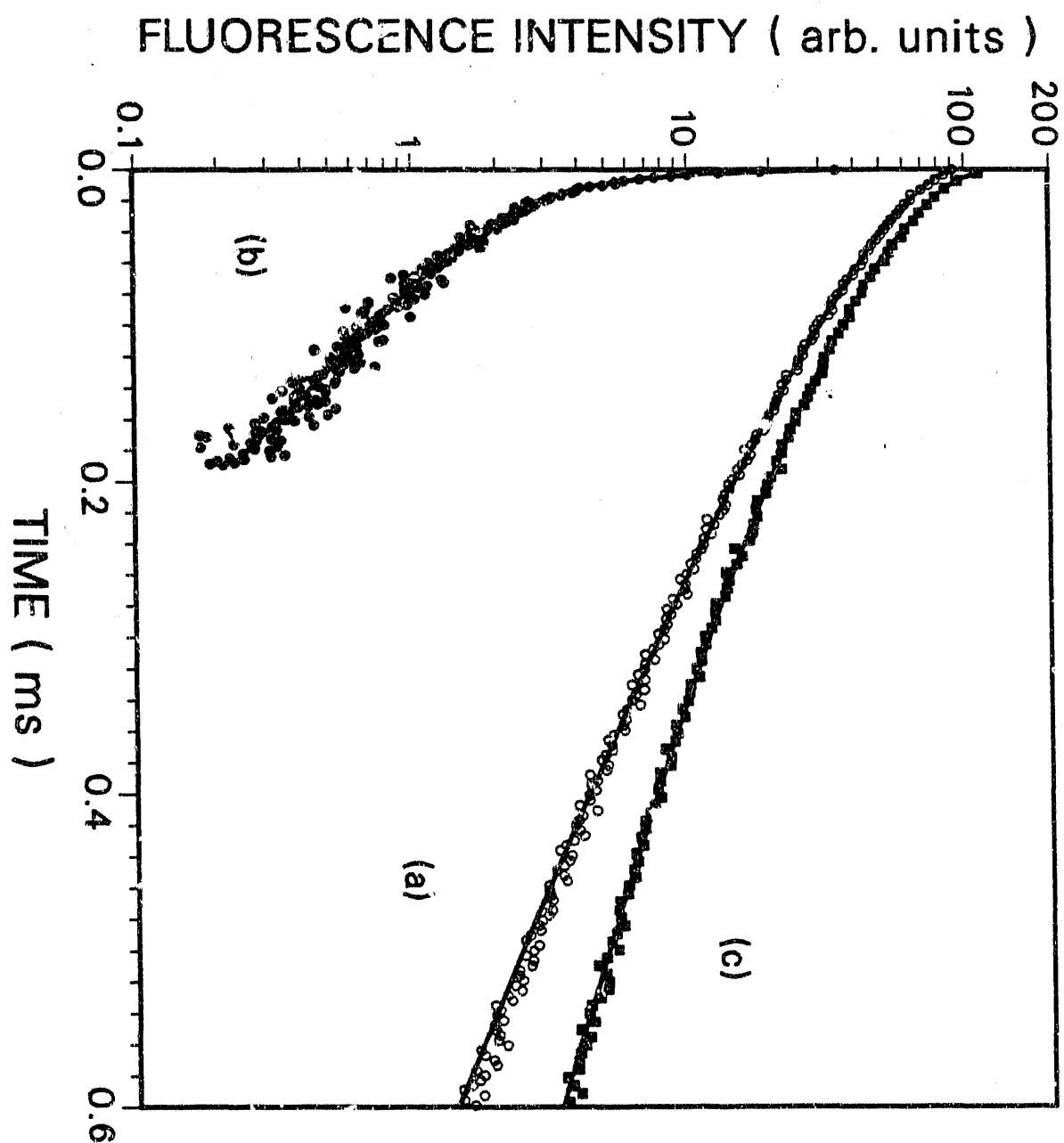
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Figure 1. Fluorescence decays of (a) 0.1 atom% Cm^{4+} in CeF_4, (b) 5 atom% Cm^{4+} in CeF_4, and (c) 0.05 atom% Bk^{4+} with 0.95 atom% Cf^{4+} in CeF_4, all at 4 K. Solid curve (a) results from fitting the data using a cross relaxation model [Eq. (1)], and solid curves (b) and (c) correspond to an exciton-exciton annihilation model incorporating trapping [Eq. (3)].

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