Picosecond excited state absorption studies of isothiocyanato complexes of Cr(III) in solution[1,2]

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The spectra and risetimes for the doublet excited state absorption (ESA) of *t*-$[Cr(NH_3)_2(NCS)_4]^-$ (Reineckate ion), $[Cr(NCS)_6]^{3-}$, and *t*-$[Cr(en)_2(NCS)_2]^+$ have been measured at picosecond times in several solvents. The ESA spectra observed after approximately one half the risetimes showed no measurable change with time. The result is consistent with vibrational relaxation times which are comparable to or faster than the risetimes. The ESA risetimes for Reineckate ion and *t*-$[Cr(en)_2(NCS)_2]^+$ were found to be fastest in hydroxylic solvents and slowest in non-hydroxylic solvents. No such solvent trend was found for $[Cr(NCS)_6]^{3-}$. Possible photophysical models to account for the observed solvent-dependent risetimes are discussed. Kinetic simulations based on a quasi four-level model which explicitly includes the pump pulse function are reported.

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On a mesuré les spectres et les temps d'apparition de l'absorption de l'état excité du doublet (AEE) de *t*-$[Cr(NH_3)_2(NCS)_4]^-$ (ion de Reineckate), de $[Cr(NCS)_6]^{3-}$ et de *t*-$[Cr(en)_2(NCS)_2]$ dans des temps de l'ordre de la picoseconde et dans plusieurs solvants. Les spectres observés pour l'AEE après approximativement la moitié du temps d'apparition ne révèlent pas de changements mesurables avec le temps. Le résultat est en accord avec des temps de relaxation vibrationnelle qui sont comparables ou plus élevés que les temps d'apparition. On a trouvé que les temps d'apparition de l'AEE de l'ion de Reineckate et du *t*-$[Cr(en)_2(NCS)_2]$ sont plus rapides dans les solvants hydroxyliques et plus lents dans les solvants non hydroxyliques. On n'a pas trouvé une telle tendance avec le $[Cr(NCS)_6]^{3-}$. On discute des modèles photophysiques susceptibles d'expliquer l'influence du solvant sur les temps d'apparition. On rapporte les simulations cinétiques basées sur le quasi modèle à 4 niveaux qui comprend explicitement la fonction de pompe à pulsation.

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1. Introduction

In O_h symmetry Cr(III) complexes, the photochemistry and photophysics are associated with two close-lying states: a $^4T_{2g}$ and a ^2E_g state, the former being "distorted" with respect to the ground state. The spin-forbidden ^2E_g state, which is usually the lowest energy and the emitting state, has been extensively studied (1–4). However, owing to the close but unquantified proximity of the two excited states, the respective roles of the quartet and doublet states in photoreactions and in the decay of the doublet state has not yet been unambiguously delineated for most systems (3–8).

Although the vibrationally relaxed doublet state of Cr(III) complexes is well characterized, data at early times leading to the formation of the relaxed doublet are sparse. Notable exceptions are the picosecond excited state absorption (ESA) studies by Windsor and co-workers (9, 10). Doublet risetimes of 16–22 ps for three Cr(III) isothiocyanato complexes in H_2O were reported. It was suggested that the risetime may reflect a combination of intersystem crossing and relaxation within the doublet manifold.

The influence of solvent on the primary photophysical/photochemical rates following population of the Franck–Condon quartet state is unclear. Provided that intersystem crossing occurs after substantial quartet relaxation, significant change from the Franck–Condon geometry and solvent reorganization can occur. The role of solvent in the relaxation process might involve a non-specific property such as viscosity or a specific solvent–ligand interaction such as hydrogen bonding.

To gain further understanding of the primary processes involved in Cr(III) complexes, we have measured the doublet ESA spectra and risetimes of $[Cr(NCS)_6]^{3-}$, *t*-$[Cr(NH_3)_2(NCS)_4]^-$ (Reineckate ion, R^-), and *t*-$[Cr(en)_2(NCS)_2]^+$ in a variety of solvents and analyzed these results in terms of the rate constants associated with the quartet and doublet states. Kinetic simulations in terms of a quasi four-level model are reported.

2. Experimental

The Nd/glass picosecond absorption apparatus used (11) was similar to that reported earlier (12) but has been significantly improved. The 5 cm D_2O cell used to produce the 1.06 u superbroadened picosecond probe beam (13, 14) was reduced to 2.0 cm. This reduction in cell length resulted in a probe beam with a reduced chirp (measured 6 ps) (15) and which was spectrally more uniform and reproducible across the echelon. The equally stepped echelon used previously was replaced with a quartz 5-step echelon having relative step differentials of 50, 5, 5, 20, and 50 mm (= 81.3, 8.13, 8.13, 32.5, and 81.3 ps at 5300 Å). The first step provided a "$-\infty$" time spectrum in advance of the 5300 Å pump pulse and the last step a "$+\infty$" long time continuum reference spectrum. The spectra were recorded on Royal Pan-X sheet film which was pushed-developed (in HC-110B) to yield an effective ASA of 3000, with a measured γ of 0.64 and a linear density range of 0.4–1.4. The film containing a set of six spectra was scanned by a microprocessor-controlled sampling microdensitometer (16). The data were smoothed by a series of Fast Fourier transform based algorithms (11) to yield a sequence of related density spectra. A selected

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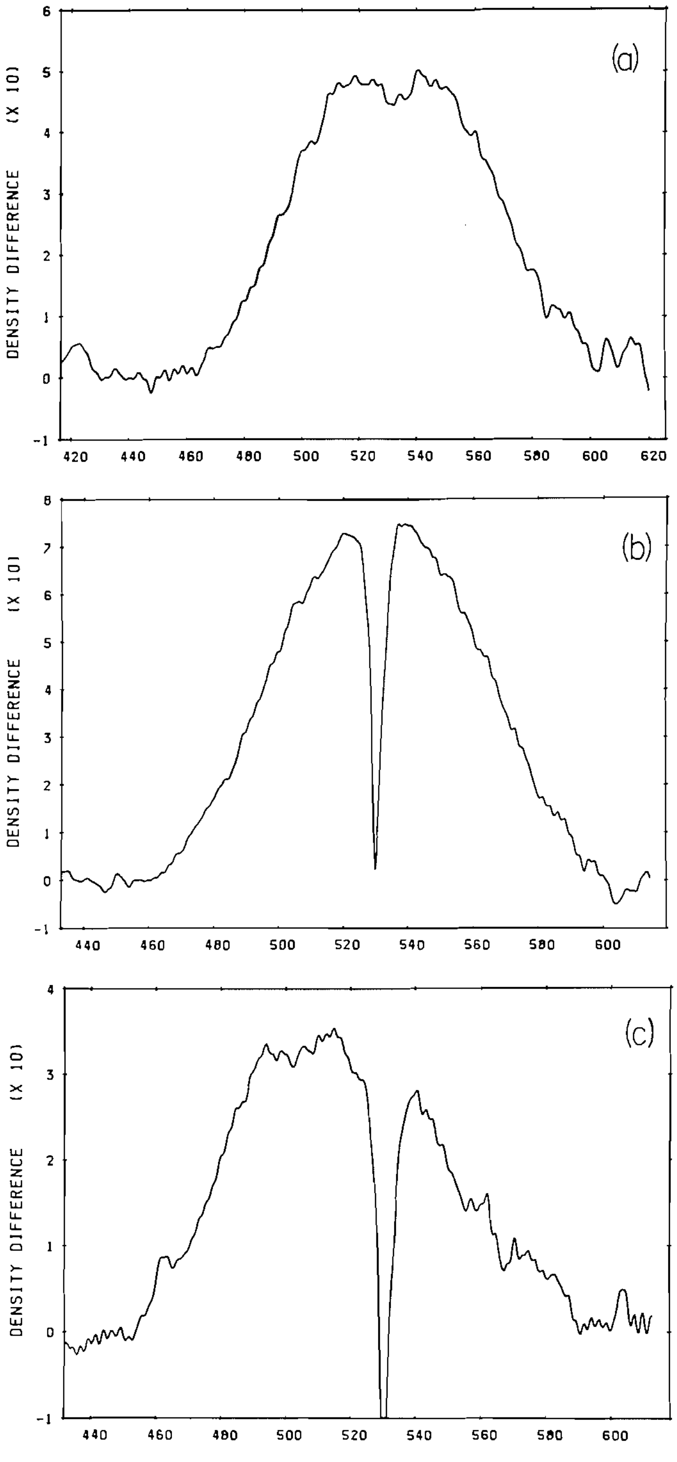

FIG. 1. Transient absorption spectra of R$^-$ in (*a*) in DMF at 51 ps; (*b*) in acetone at 160 ps; and (*c*) H_2O at 57 ps.

wavelength range of the transient absorption spectra was integrated and used for kinetics. The relative timing of the excitation and probe pulse was determined to within 3 ps by a sensitive zero-background null method based on the Kerr gating of the continuum pulse (15).

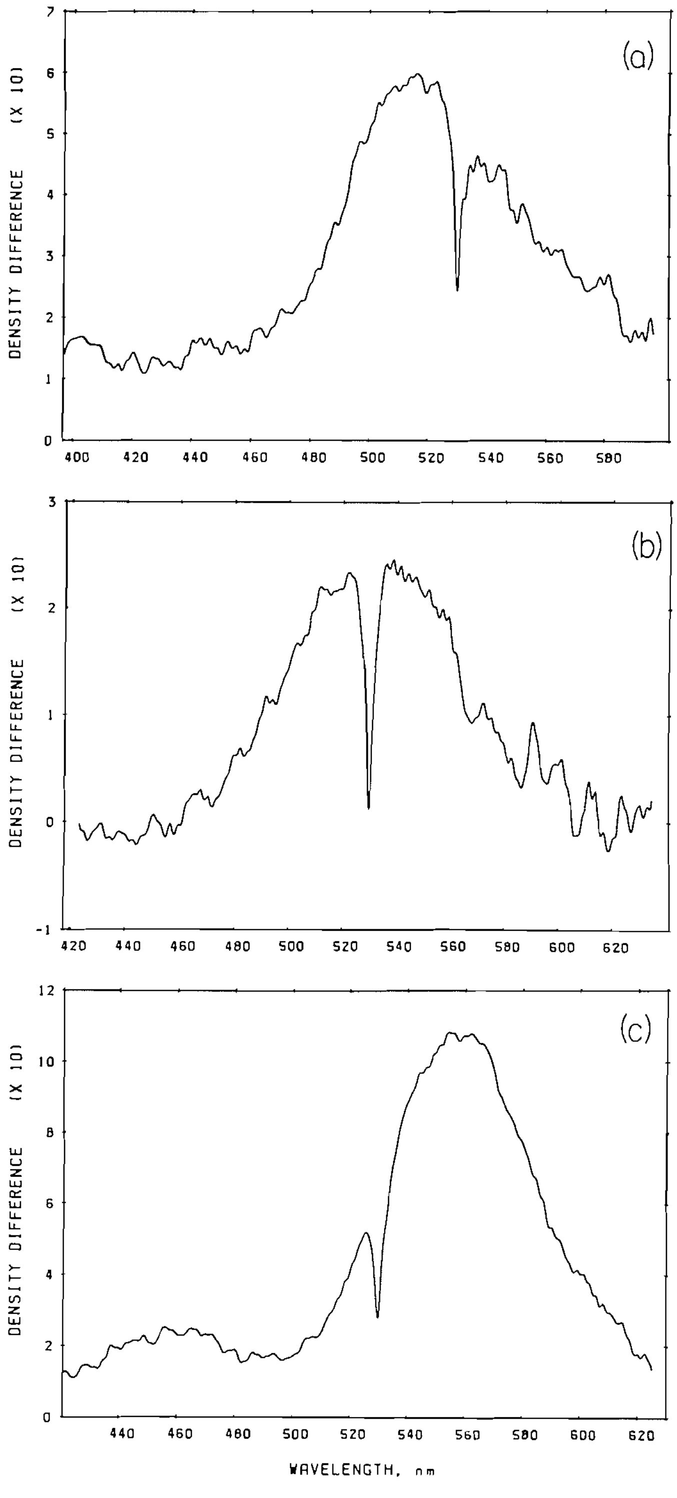

FIG. 2. Transient absorption spectra of some isothiocyanato Cr(III) complexes in acetonitrile solution. (*a*) $[Cr(NCS)_6]^{3-}$ at 47 ps; (*b*) R$^-$ at 71 ps; and (*c*) $[Cr(en)_2(NCS)_2]^+$ at 43 ps.

3. Results

Transient absorption spectra were observed when $[Cr(NCS)_6]^{3-}$, R$^-$, and *t*-$[Cr(en)_2(NCS)_2]^+$ in various solvents were excited by picosecond laser pulses at 530 nm. Typical spectra recorded at probe delay times of less than 100 ps are shown in Figs. 1 and 2, and the transient absorption maxima recorded in Table 1. The transient absorption band observed for both R$^-$ and *t*-$[Cr(en)_2(NCS)_2]^+$ showed a noticeable solvent dependence (shifted towards the blue in water), whereas the symmetric complex $[Cr(NCS)_6]^{3-}$ did not. The intensities of the transient absorption bands for R$^-$ and $[Cr(NCS)_6]^{3-}$ were comparable, independent of solvent, and approximately two times less intense than that for *t*-$[Cr(en)_2(NCS)_2]^+$. We were

TABLE 1. Absorption maxima of transient[a]

Complex	Solvent	$\lambda_{max,nm}$
R^-	CH_3CN	533, (525)[b]
	DMF	531
	CH_3COCH_3	530
	CH_3CH_2OH	530
	D_2O	510
	H_2O	510
	CH_3CN/H_2O (X_{H_2O}=0.84)	(521)[c]
t-$[Cr(en)_2(NCS)_2]^+$	CH_3CN	558, 456
	H_2O	530
$[Cr(NCS)_6]^{3-}$	CH_3CN	516
	DMF	520
	H_2O	520
	Glycerol/H_2O (65% by wt.)	516
	Alcohol glass (100 K)	(538)[d]
	EPA (77 K)	(542)[e]

[a] Figures in parentheses are the literature values for the doublet excited state.
[b] Reference 20.
[c] Reference 19.
[d] Reference 17.
[e] Reference 18.

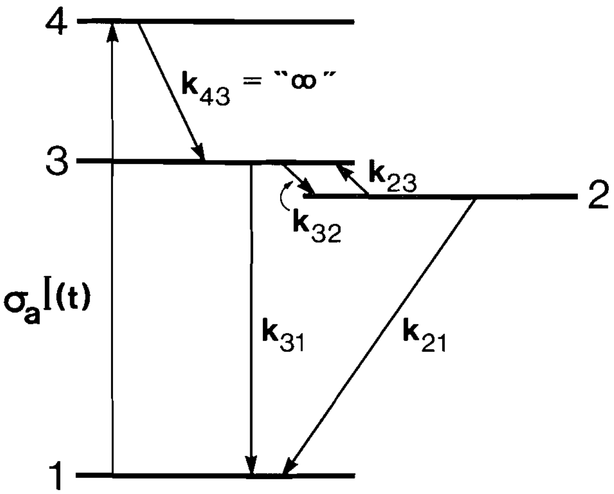

FIG. 3. Schematic of a quasi four-level system.

unable to detect a change in any of the transient absorption spectra with time. Any change was therefore either small or very rapid ($t < 1/2$ risetime), or both.

Buildup of the transient absorption for the complexes varied from a few picoseconds to tens of picosecond depending upon the complex and solvent. During the excitation pulse, formation of the transient population will be integral functions of the excitation pulse. Therefore, for those transients rising within one or two laser pulse widths (6–12 ps), the pump pulse function cannot be ignored in any kinetic analysis. For a quasi four-level system (Fig. 3), we have for the populations of the three states:

$$[1]\quad \dot{n}_1 = -\sigma_a I(t) n_1 + k_{31} n_3 + k_{21} n_2$$

$$[2]\quad \dot{n}_2 = k_{32} n_3 - (k_{23} + k_{21}) n_2$$

$$[3]\quad \dot{n}_3 = \sigma_a I(t) n_1 + k_{23} n_2 - (k_{31} + k_{32}) n_3$$

where σ_a is the absorption cross section (see Fig. 3). Empirically, a satisfactory fit of the data was obtained with the function

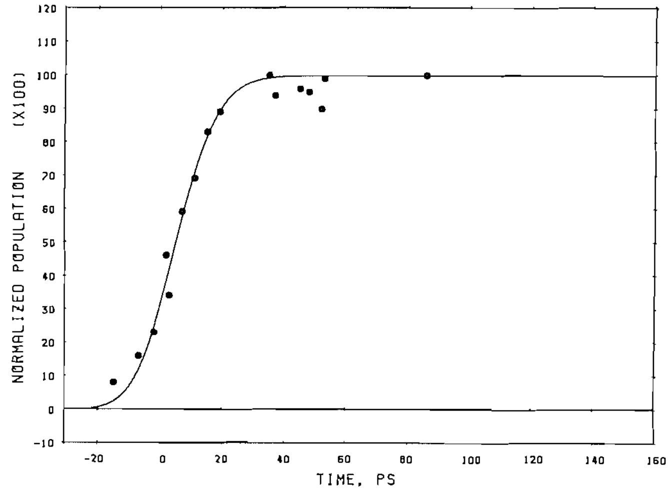

FIG. 4. Transient ESA buildup for R^- in D_2O. The solid curve was calculated from eq. [4] (see text).

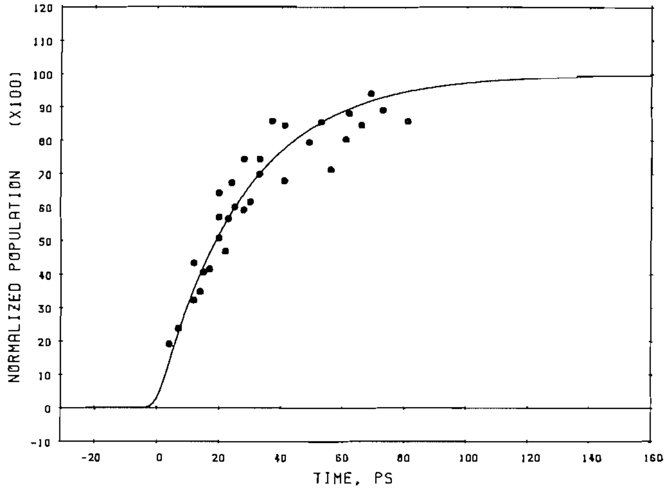

FIG. 5. Transient ESA buildup for R^- in acetone. The solid curve was calculated from eq. [4] (see text).

$$[4]\quad n_2(t) = 1/2(T\sqrt{\pi} I_0 \sigma_a n_1)\{\exp(-k_{32}t + k_{32}{}^2T^2/4) \times [1 + \mathrm{erf}(t/T - k_{32}T/2)] - [1 + \mathrm{erf}(t/T)]\}$$

which can also be derived from the three coupled differential equations for the conditions in which $\dot{n}_1 = 0$; $k_{31} = k_{21} = k_{23} = 0$; and for the Gaussian pulse

$$[5]\quad I(t) = I_0[\exp(-t^2/T^2)]$$

where I_0 is the peak photon flux of the pump pulse. The data were fitted to eq. [4] by trial values of the parameter T and k_{32} to find the smallest value of the sum of squares of the residuals between the calculated and observed values of n_2 for the set of data. The parameter T in the Gaussian pulse is related to τ, the full-width at half-maximum (FWHM) by $T = \tau/2\sqrt{\ln 2}$. The kinetics for formation of the transient from R^- in D_2O and acetone are shown in Figs. 4 and 5. The solid curves are calculated from eq. [4]. Risetime results are recorded in Table 2. The most significant variations in the risetimes were found for R^- which varied from less than 6 ps in H_2O to 29 ps in DMF. The risetimes of R^- in H_2O appeared to be faster than

TABLE 2. Risetime of transient[a]

Complex	Solvent	τ, ps
R^-	CH_3CN	18
	DMF	29
	CH_3COCH_3	27
	CH_3CH_2OH	8
	D_2O	6 (11)[b]
	H_2O	<6 (22)[b] (<5)[c]
t-$[Cr(en)_2(NCS)_2]^+$	CH_3CN	15
	H_2O	9 (16)[b]
$[Cr(NCS)_6]^{3-}$	CH_3CN	5
	DMF	10
	H_2O	11 (16)[b]
	Glycerol/H_2O (65% by wt.)	6

[a] Figures in parentheses are literature values.
[b] Reference 10.
[c] Reference 9.

D_2O but both risetimes are fast and close to the temporal width of the laser pulse. While it is possible to obtain reliable risetimes to within a fraction of the laser pulse width using our data fitting procedure, the requirement of low jitter in the width of the pulse from shot to shot is presently one of the main, though not insurmountable, difficulty towards realizing a shorter time resolution.

4. Discussion

The transients observed for the three chromium complexes have been assigned to excited state absorption from the doublet state on the basis of the agreement between the transient absorption and phosphorescence lifetimes (7–10, 17–21). The ESA risetime for R^- and t-$[Cr(en)_2(NCS)_2]^+$ were found to be fastest in hydroxylic solvents and slowest in non-hydroxylic less polar solvents. No such solvent trend was found for the symmetric $[Cr(NCS)_6]^{3-}$. The risetime in glycerol/water was not significantly different from the less viscous solvents. This observation could be interpreted in two ways: either (*1*) bulk viscosity does not correlate with the difficulty of solvation shell rearrangement because of the presence of few glycerol molecules in the solvent sphere of the complex ion, or (*2*) solvent-restricted quartet relaxation for $[Cr(NCS)_6]^{3-}$ is unimportant in the photophysics.

The absence of observable time dependent changes in the ESA spectra after approximately one half the risetimes is consistent with vibrational relaxation times which are comparable to or faster than the risetimes. Absorption from vibrationally unrelaxed states of the doublet appears as "hot band" absorption. In the case of very fast crossing the unrelaxed doublet followed by slow vibrational relaxation to the zero level of the doublet, the shift is given by the difference in energy between the pump wavelength and 0–0 transition between the doublet and the ground state. The shift is substantial for the present complexes. In the case of reduced hot band population due to substantial vibrational relaxation, the shift is less evident. Another caveat to the above conclusion is the remote possibility of the effects of vibrational relaxation being masked by compensating time-dependent solvation effects.

The simplest interpretation of the observed solvent-dependent ESA risetimes is to assume that the risetime is governed by the rate of intersystem crossing from the quartet manifold. An intersystem crossing model involving "prompt" crossing from the unrelaxed quartet levels and a slower crossing rate is expected to give a risetime with a slow and fast regime. We found no kinetic evidence for this. In the case of R^- in water, buildup of the doublet was complete after less than 20 ps; a slower component, which would be noticeable, was not observed.

A possible explanation for a solvent-dependent intersystem crossing in non-symmetrically substituted complexes such as the R^- ion (D_{4h} symmetry) was suggested by Orlandi and Siebrand (22). The model assumes rapid vibrational relaxation and redistribution and that the solvent dependent electrostatic field of the ligand influences the energies of the quartet states. Because of a lowering in symmetry for O_h to D_{4h} because of the unequal ligands, ${}^4T_{2g}$ splits into ${}^4E + {}^4B_{2g}$. The splitting, ϵ, is assumed to be solvent dependent. On the basis of symmetry arguments, the coupling between the ${}^4E$ and ${}^2E$ is zero but coupling between the ${}^4B_{2g}$ and ${}^2E$ is non-zero. For the case in which the ${}^4E$ is lower in energy than the ${}^4B$ state, the relative population of the ${}^4B_2$ and ${}^4E$ states differ by the Boltzmann factor $\exp(-\epsilon/kT)$, so that the rate of intersystem crossing

[6] $k_{\mathrm{isc}} = 2\pi/\hbar|\langle {}^2E|H_{so}|{}^4B_2\rangle|^2 \exp(-\epsilon/kT)\rho_E$

is solvent dependent through ϵ. For R^-, owing to solvation of the charged NCS groups, ϵ is expected to be smaller in polar than non-polar solvents. For the symmetric $[Cr(NCS)_6]^{3-}$ complex, no solvent effect is predicted. For the cationic t-$[Cr(en)_2(NCS)_2]^+$ complex where the relative energies of the ${}^4B_{2g}$ and ${}^4E$ states would be the opposite that of R^-, no solvent effect is predicted. The Orlandi–Siebrand model correctly predicts the trend of the results for R^- and $[Cr(NCS)_6]^{3-}$ but not for t-$[Cr(en)_2(NCS)_2]^+$, where a small solvent effect is observed. In the case of the t-$[Cr(en)_2NCSF]^+$, differential quenching and quantum yield evidence does indeed suggest the participation of two quartet states (23).

Hollebone and co-workers (24) have described a model in which photochemistry and intersystem crossing competes with vibrational relaxation and redistribution. In this model, population and decay on a specific nuclear coordinate governs the photophysical and photochemical behaviour. Solvents which hydrogen bond to the ligands could couple to vibrational coordinates active in intersystem crossing. The present data are consistent with the view that hydrogen-bonding is an important influence on the rate of intersystem crossing.

Thus far, we have assumed that the risetime is governed only by the rate constant for intersystem crossing, k_{32}. To investigate the sensitivity of the *form* of the normalized risetime function to other rate constants, numerical simulations were carried out based on the quasi four-level system (Fig. 3). The system can be characterized by the equations:

[7*a*] $\dot{n}_2(x) = R_5[n_3 - (R_2 + R_3)n_2]$

[7*b*] $\dot{n}_3(x) = R_5[R_4F(x)(1 - n_2 - n_3) + R_3n_2 - (1 + R_1)n_3]$

[8] $n_1 + n_2 + n_3 = 1$

and the five dimensionless parameters:

[9*a*] $R_1 = k_{31}/k_{32}$

[9*b*] $R_2 = k_{21}/k_{32}$

[9*c*] $R_3 = k_{23}/k_{32}$

[9*d*] $R_4 = \sigma_a I_0/k_{32}$

[9*e*] $R_5 = \tau k_{32}$

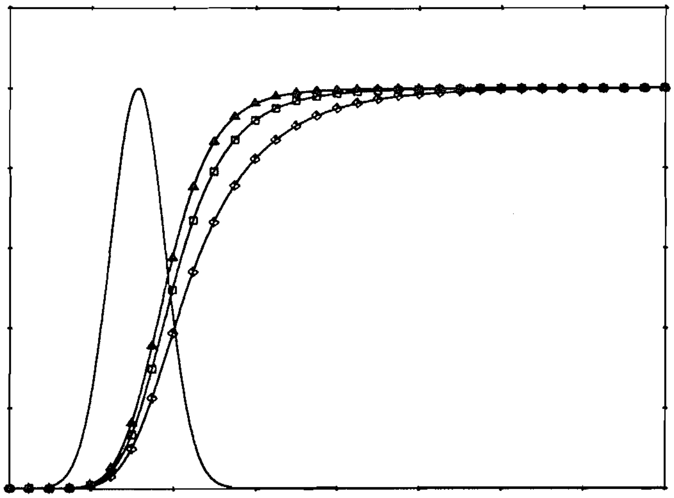

FIG. 6. Calculated normalized $n_2(x)$ vs. x from numerical simulation (see text). $R_2 = 0, R_3 = 0, R_4 = 0, R_5 = 1.0$. (△) $R_1 = 0$; (□) $R_1 = 0.5$; (◇) $R_1 = 1.0$. The curve without symbol is the Gaussian pump function $F(x)$ vs x.

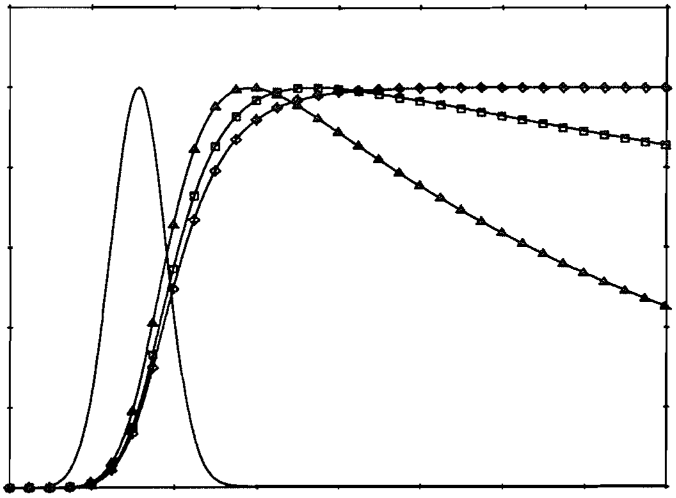

FIG. 8. Calculated normalized $n_2(x)$ vs. x from numerical simulation. $R_2 = 0, R_3 = 0.5, R_4 = 0, R_5 = 1.0$. (△) $R_1 = 0$; (□) $R_1 = 0.1$; and (◇) $R_1 = 0.5$. The curve without symbol is the pump pulse function $F(x)$ vs. x.

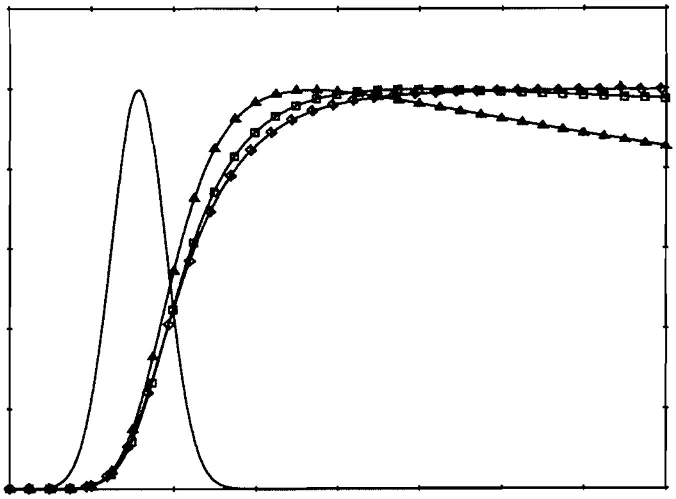

FIG. 7. Calculated normalized $n_2(x)$ vs. x from numerical simulation (see text). $R_2 = 0, R_3 = 0.1, R_4 = 0, R_5 = 1.0$. (△) $R_1 = 0$; (□) $R_1 = 0.1$; (◇) $R_1 = 0.5$. The curve without symbol is the pump pulse function $F(x)$ vs. x.

where τ is the full-width at half-maximum of the pump pulse, and I_0 is the maximum intensity of the pump pulse $I(t) = I_0F(x)$, $(0 < F(x) < 1$ for $\tau > 0)$, and $x = t/\tau$. The coupled first-order differential equations, [7*a*] and [7*b*], which explicitly include the pump function, were solved using Hamming's modified predictor-corrector method (25). The time-dependent population of level 2, $n_2(t)$, was calculated for a Gaussian pump pulse and for the parameter $R_2 = 0$, since decay of the doublet state is known to be negligible over the range of the dimensionless time variable $x = t/\tau$ of the simulation. Details of a general treatment of the quasi four-level system, driven by an arbitrary laser pulse, will be reported in a future publication. The normalized population of level 2 together with the laser pulse function is shown in Figs. 6–8. The simulation shows that: (*1*) For no reverse reaction ($k_{23}/k_{32} = 0$), level 2 builds up more rapidly as k_{31} is increased. (*2*) The rate of buildup of level 2 is also increased when the reverse reaction is included ($k_{23}/k_{32} > 0$). In this case, the effect of k_{31} is to cause a decay in the population of level 2 after the maximum population is reached.

In the present study, no doublet state decay has been observed over the range of time studied. Therefore the rate of back intersystem crossing from the initially formed vibrationally excited doublet state appears to be significantly slower than the rate of intersystem crossing or vibrational relaxation. The simulation suggests that the conditions $k_{23}/k_{32} > 0.1$ and $k_{31}/k_{32} > 0.1$ cannot be both true. Less can be said about the relative rates of decay and intersystem crossing of the quartet state. There are two consequences of quartet decay in competition with intersystem crossing: the yield of doublet, and the form of the doublet population vs. time function (especially in the rising part) are affected. If the rate constant for intersystem crossing (k_{isc}) is much greater than other quartet decay channels (k_{Q}), then the doublet yield will not be very sensitive to changes in k_{Q}. Current data on the relative doublet yield in various solvents are consistent with this condition, although we cannot exclude the possibility on the basis of doublet yield alone, that both k_{Q} and k_{isc} are affected by solvent.

As the simulation shows, the precise form of the doublet population function is sensitive to five kinetic parameters R_1–R_5. Of the five, R_4 is constant and R_5 can be controlled. The parameter R_2, which measures decay directly from the doublet state, is known to be small compared with R_1 and R_3. With sufficiently accurate data, it is thus possible to obtain the rate constants for quartet decay and back intersystem crossing relative to that for intersystem crossing by fitting the data with the exact form of the population function. The realization of this goal awaits the obtention of highly accurate kinetic data which requires close control of the laser parameters and possibly signal averaging.

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