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Efficiency of Intersystem Crossing to the Lowest Excited State of Chromium Polypyridyls Determined by Using Pulsed Photoacoustic Microcalorimetry

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A simple photoacoustic detection system for determining intersystem crossing yields, Φ_{isc}, of inorganic systems is described. Values found for Φ_{isc} of $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$, and $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$ are 0.93, 0.95, 0.73, and 1.04, respectively. This is in excellent agreement with the reported values of 0.95–1.0 for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ based on other techniques. This technique has also been used to determine that there are long-lived ($\tau > 10$ ns) upper excited states or other high-energy species produced that prevent rapid relaxation to the $^2E/^2T$ manifold following excitation of $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}Me_2phen)_3^{3+}$. Without resorting to deconvolution techniques, this method can be used on systems that have rapid relaxation ($\tau < 1$ ns) of the upper excited states and lifetimes >5 μs for the lowest energy excited state when a 5-MHz transducer is used for detection of the photoacoustic signal.

Introduction

The excited-state behavior of chromium(III) polypyridyls has been the object of many investigations and continuing discussion.[1–6] Thus, the assignment of the principal absorption features has continued to evolve,[5,6] and the issue of whether the upper states relax rapidly (in the picosecond regime) or slowly ($\tau \geq 1$ ns) is still being debated.[3,4] In a recent contribution to this debate, Serpone and Hoffman have reported evidence for three short-lived transients, which they attribute to high-energy ligand-centered and metal-centered excited states. The longest lived upper state has been reported to decay to the lowest energy excited state, $^2T/^2E$, in a few nanoseconds.[4] These upper-state relaxation processes are believed to efficiently populate the $^2T/^2E$ state, and the net quantum yields (Φ_{isc}) of the lowest energy excited states have been estimated as 0.95[7] or 1.0[8,9] for $Cr(phen)_3^{3+}$ and 1.0[8,9] for $Cr(bpy)_3^{3+}$.

Direct measurements of intersystem crossing yields (Φ_{isc}) are rare. The relatively new technique of pulsed photoacoustic microcalorimetry can be used to directly monitor the heat released from such upper-state relaxation processes.[10–13] This information, when combined with the energy of excitation and the energy of the metastable excited-state "product" (the $^2E/^2T$ state in Cr(III) complexes), can be readily used to determine Φ_{isc}.[10–13] In addition to being the most direct means of determining values of Φ_{isc}, the manner in which the excited-state relaxation processes couple to the characteristic piezoelectric transducer frequency can provide information[14] which in principle complements that obtained in the flash photolysis experiments. In this paper we describe a simple pulsed photoacoustic system and its use in determination of Φ_{isc} for several polypyridyl complexes of Cr(III).

Experimental Section

Materials and Techniques. Perchlorate salts of the chromium(III) polypyridyls were available from previous studies in this laboratory.[6,15] Anthracene, fluorenone, xanthone, and bis(*o*-methylstyryl)benzene (bis-msb) were twice recrystallized from ethanol. Rhodamine 6G was obtained from Exciton Chemical Co. Inc. and used without further purification. Absolute ethanol was also used without further purification but was filtered with a fine-frit funnel.

A schematic of the photoacoustic detection system is shown in Figure 1. Optically thin (Abs < 0.11) sample solutions were pumped by 15-ns-duration pulses of 308-nm radiation produced from a Lambda Physik EMG 102 excimer laser. The unattenuated beam energy was approximately 130 μJ in a spot size of diameter 1 mm (1.55×10^{14} photons mm^{-2}/pulse). The mean intensity of the laser was constant over the duration of each experiment and had peak to peak fluctuations of 5%.

The narrow-band photoacoustic transducer (Panametrics Model A112) had a resonant frequency, υ, of 5 MHz and relaxation time, τ_0, of 3.5 μs (i.e. time taken for signal to be completely damped) and was used with a preamp (Panametrics Model 5670) of gain 40 dB. A transient recorder (Gould Biomation Model 4500) sampled the preamp output with an A/D rate of 10 ns/sample. The experimental observable was the voltage difference between the crest of the first positive peak maximum and the trough of the following peak (i.e. the initial peak amplitude). The transducer (diameter 0.25 in.) was pressed against the side of a 1-cm fluorescent cell. The acoustic coupling was enhanced by using a thin layer of silicon grease between the cell and the transducer. Since maintaining a constant cell–transducer–laser beam geometry is critical for an accurate interpretation of the results, all optical components were rigidly clamped to an optical bench. All experiments were carried out at ambient temperature and all solutions were air-equilibrated, since we were only interested in fast processes (as defined by the transducer response) and all the complexes had lifetimes >10 μs. For all samples, we observed waveforms that were stable and reproducible from one laser shot to the next. The S/N was improved 8-fold by averaging 64 waveforms in the transient recorder before recording the data for each determination.

Treatment of Data

The following equation shows how a pressure transducer signal reflects heat deposition if it is assumed that the acoustic wave is generated by a point source and observed by a point detector:[10]

$$V_t = \frac{h_0 A \upsilon/\tau}{4\pi r_0[\upsilon^2 + (1/\tau')^2]}\left\{e^{-t/\tau} - e^{-t/\tau_0}\left[\cos(\upsilon t) - \frac{1}{\upsilon\tau'}\sin(\upsilon t)\right]\right\} \tag{1}$$

where V_t is the measured signal amplitude at time t, $h_0 = \eta_{nr}E_1(1 - 10^{-A})$ is the heat deposition, η_{nr} is the efficiency of nonradiative emission, E_1 is the laser energy ($nh\upsilon$), A is the sample absorbance, υ is the resonant frequency of the transducer (i.e. 5 MHz), τ is the lifetime of the transient, τ_0 is the relaxation time of the transducer (i.e. 3.5 μs), r_0 is the distance between the laser beam and the transducer, and $1/\tau' = 1/\tau - 1/\tau_0$.

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[1] Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* **1981**, *39*, 121.

[2] Serpone, N.; Hoffman, M. Z. *J. Chem. Educ.* **1983**, *60*, 853.

[3] (a) Magde, D.; Rojas, G. E. *J. Phys. Chem.* **1987**, *91*, 689. (b) Rojas, G. E.; Dupoy, C.; Sexton, D. A.; Magde, D. *J. Phys. Chem.* **1986**, *90*, 87.

[4] Serpone, N.; Hoffman, M. Z. *J. Phys. Chem.* **1987**, *91*, 1737.

[5] Ohno, T.; Kato, S.; Kaizaki, S.; Hanzaki, I. *Chem. Phys. Lett.* **1983**, *102*, 471.

[6] Ryu, C. K.; Endicott, J. F. *Inorg. Chem.*, in press.

[7] Kane-Maguire, N. A. P.; Langford, C. H. *Inorg. Chem.* **1976**, *15*, 464.

[8] Serpone, N.; Jamieson, M. A., Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* **1980**, 1006.

[9] An early estimate of 0.21 for $Cr(phen)_3^{3+}$ seems less plausible (Bolleta, F.; Maestri, M.; Balzani, V. *J. Phys. Chem.* **1976**, *80*, 2499).

[10] Rothberg, L. J.; Simon, J. D.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464.

[11] Rothberg, L. J.; Bernstein, M.; Peters, K. S. *J. Chem. Phys.* **1983**, *79*, 2569.

[12] Komorowski, S. J.; Grabowski, Z. R.; Zielenkiewicz, W. *J. Photochem.* **1985**, *30*, 141.

[13] Grabowski, J. J.; Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 4615.

[14] Rudzki, J. E.; Goodman, J. C.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849.

[15] Endicott, J. F.; Ramasami, T.; Tamilarasan, R.; Lessard, R. B.; Ryu, C. K. *Coord. Chem. Rev.* **1987**, *77*, 1.

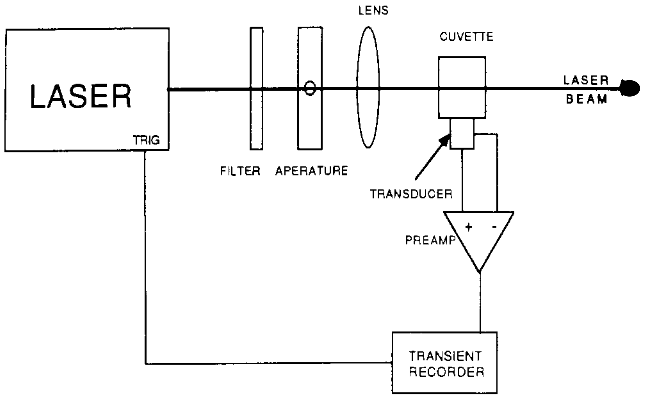

Figure 1. Schematic of the photoacoustic detection system used in this study.

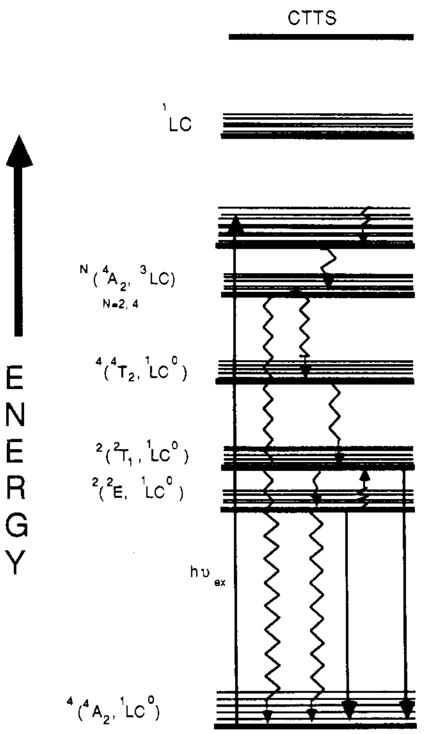

Figure 2. Proposed energy level diagram showing possible relaxation pathways for $Cr(NN)_3^{3+}$ complexes when excited into the $^4(^4A_2, ^3LC)$ band by light of energy 32 468 cm^{-1}. The notation $^N(^4A_2, ^3LC)$ is used to describe the excited states in which there is exchange-mediated spin–spin coupling between the ($^4A_2$) Cr(III) ground state and the ligand-centered state of triplet spin multiplicity (see ref 6). The net spin multiplicity, *n*, of such states is determined by the effective molecular symmetry and the spin multiplicities of the metal and ligand centers.

For transients whose lifetimes are much shorter than the time-resolved detection limits of the transducer (i.e. $\tau < 10$ ns), eq 1 reduces to

$$V_t = K\eta_{\text{pnr}}E_{\text{abs}} \tag{2}$$

at time *t*. Here η_{pnr} is the efficiency of prompt ($\tau < 1$ ns) nonradiative emission, *K* is an experimental constant for all prompt nonradiative processes and is determined at the peak maximum of the waveform (i.e. experimental observable), and $E_{\text{abs}} = E_{\text{l}}(1 - 10^{-A})$ is the absorbed photon energy.

For a Cr^{3+} upper excited state (see Figure 2) that relaxes rapidly to a relatively long-lived ($\tau > 10$ μs) doublet state and undergoes no upper-excited-state photochemistry, the following equation defines the efficiency of heat released in prompt nonradiative processes of all the upper excited states:[11-13]

$$\eta_{\text{pnr}} = 1 - \Phi_{\text{fl}}\frac{\upsilon_{\text{fl}}}{\upsilon_{\text{ex}}} - \Phi_{\text{isc}}\frac{E_{\text{s}}}{h\upsilon_{\text{ex}}} \tag{3}$$

where Φ_{fl} is the quantum yield of fluorescence, υ_{fl} is the average frequency of fluorescence, υ_{ex} is the excitation frequency, E_{s} is the energy of the long-lived, low-energy excited state, and Φ_{isc} the quantum yield of intersystem crossing to this state. The second term represents the fraction of the absorbed energy released radiatively, while the third term represents the fraction of energy trapped in the long-lived, lowest energy doublet state. Should prompt ($\tau < 1$) photochemistry occur, then eq 3 can be modified to account for this additional process. Any photochemistry occurring from a long-lived, $\tau > 10$ μs, excited state does not alter either eq 2 or eq 3 as long as the same absorbance is observed per laser pulse.

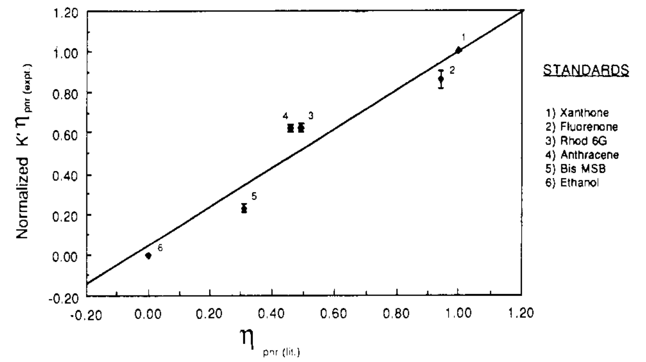

Figure 3. Instrumental calibration curve of the standards used: (1) xanthone; (2) fluorenone; (3) Rhodamine 6G; (4) anthracene; (5) bis-msb; (6) ethanol.

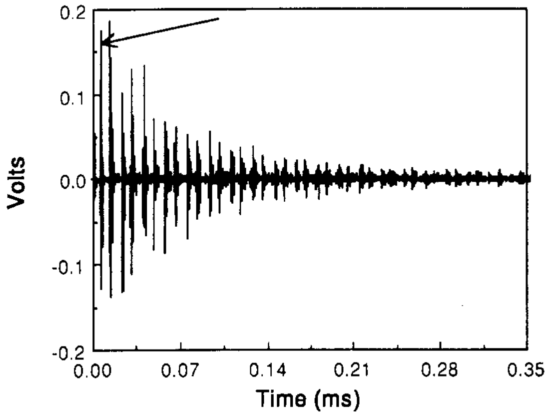

Figure 4. Transducer response resulting from prompt nonradiative decay of electronically excited $Cr(phen)_3^{3+}$. Arrow points to waveform generated from initial acoustic wave. Other waveforms are due to acoustic reflections from the cuvette walls.

Of particular advantage to the inorganic chemist is the fact that typically $\Phi_{\text{fl}} \cong 0$ for most complexes in condensed media at ambient temperature. For such a situation, only two terms contribute to eq 3. On the basis of eq 2 and 3, a simple linear relationship exists between the intersystem crossing yield and the observed photoacoustic signal.

In order to determine Φ_{isc}, a quantitative correspondence is needed between heat released, which generates an acoustic wave, and the transducer response to this wave. This is accomplished by using chemical standards whose photophysics are well-known. We used most of the same standards and their photophysical parameters as those of Peters and co-workers[10,13] but included Φ_{isc} in the calculation of $\eta_{\text{pnr(lit.)}}$ for anthracene in ethanol. Table I lists the standards used and their $\eta_{\text{pnr(lit.)}}$ values. A calibration curve, based on eq 2, is obtained by varying either the sample absorbance or the laser energy. We found that varying the laser energy, by using suitable UV filters, was faster and the data were more reproducible, resulting in correlation coefficients typically in excess of 0.99. The signal amplitude for each sample was normalized to its absorbance and plotted against % *T* of the UV filters. The slope of the curve was $KE_{\text{l}}\eta_{\text{pnr(exptl)}} = K'\eta_{\text{pnr(exptl)}}$. For each standard used the experimentally derived value, $K'\eta_{\text{pnr(exptl)}}$, was plotted against the reported value $\eta_{\text{pnr(lit.)}}$ (see Table I) in order to obtain an instrumental calibration curve. Figure 3 shows the instrumental calibration curve for the standards used. The values of $\eta_{\text{pnr(exptl)}}$ for the chromium polypyridyls were determined relative to this curve.

Results

Transducer Response to Photoacoustic Wave. Figures 4 and 5 show the response of a 5-MHz piezoelectric transducer to an acoustic wave or waves resulting from prompt nonradiative decay

Table I. Quantum Yields, Lifetimes, and Excited-State Energies Where Relevant for the Compounds Used

compd	$\eta_{pnr(lit.,min)}$	$\eta_{pnr(exptl)}$[c]	$\Phi_{isc(exptl)}$	$^2E°$, 10^{-4} cm^{-1} [e]	τ, μs[e]
ethanol	0.0	calib[b]	0		
bis-msb	0.31[a]	calib[b]	≅0		
anthracene	0.46[f]	calib[b]	≅0.72[f]	1.492[f]	
Rhodamine 6G	0.49[a]	calib[b]	≅0		
fluorenone	0.94[a]	calib[b]	≅0		
xanthone	1.0[a]	calib[b]	≅1[g]		
$Cr(bpy)_3^{3+}$	0.577[d]	0.607	0.93 (0.08)	1.374	73
$Cr(phen)_3^{3+}$	0.577[d]	0.600	0.95 (0.03)	1.374	330
$Cr(5\text{-}Cl\text{-}phen)_3^{3+}$	0.577[d]	0.693	0.73 (0.05)	1.374	180
$Cr(4,4'\text{-}Me_2bpy)_3^{3+}$	0.585[d]	0.568	1.04 (0.05)	1.347	170
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	0.585[d]	0.508	(<1)[h]	1.346	570
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	0.581[d]	0.533	(>1)[h]	1.362	570

[a] $\eta_{pnr(lit.,min)}$ was calculated by using the data in ref 10 and 13 in eq 3. [b] The standards were used to obtain the calibration curve. The scatter in data for each standard was less then 2% of the mean. [c] Obtained from instrumental calibration curve (Figure 3), with estimated errors (*t* 90%) indicated in brackets. [d] Based on eq 3 where $\Phi_{isc} = 1$ and $\Phi_{fl} \cong 0$. [e] Reference 2 and: Serpone, N.; Jamieson, M. A.; Henry, M. S.; Hoffman, M. Z.; Bolletta, F.; Maestri, M. *J. Am. Chem. Soc.* **1979**, *101*, 2907. [f] Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973. [g] At room temperature essentially all excited states of xanthone decay promptly and nonradiatively to the ground state. [h] On the basis of eq 2 and 3, nominal values of Φ_{isc} for $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}Me_2phen)_3^{3+}$ were 1.19 (±0.07) and 1.11 (±0.04), respectively. These equations and the results obtained are therefore not applicable for these two complexes due to slow (τ > 15 ns) upper-excited-state chemistry. See text for discussion.

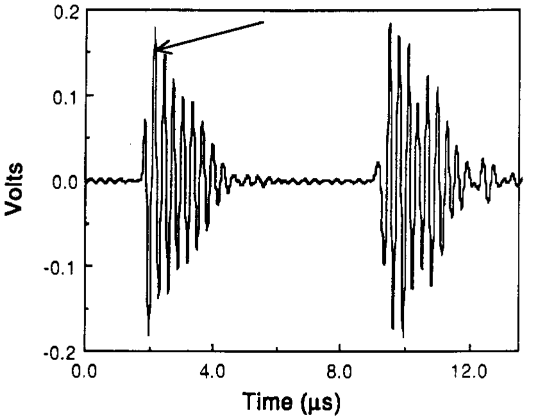

Figure 5. Transducer response due to the initial and first reflected acoustic waves for $Cr(phen)_3^{3+}$. Note the expansion of the time scale from Figure 4.

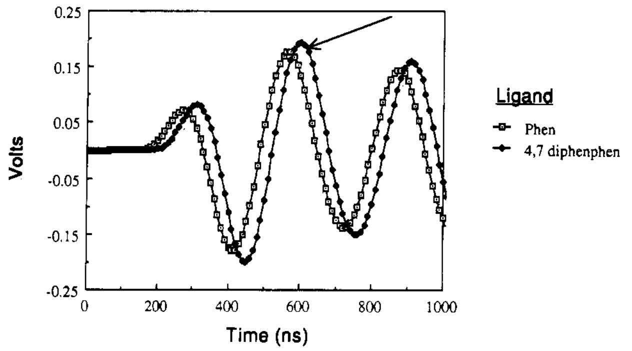

Figure 6. Transducer response resulting from prompt nonradiative decay of electronically excited $Cr(phen)_3^{3+}$ and $Cr(4,7\text{-}Ph_2phen)_3^{3+}$. The peak maxima of $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}Me_2phen)_3^{3+}$ (not shown) are slightly phase-shifted relative to $Cr(phen)_3^{3+}$. The signal amplitudes are not normalized to sample absorbance. Note the greatly expanded time scale.

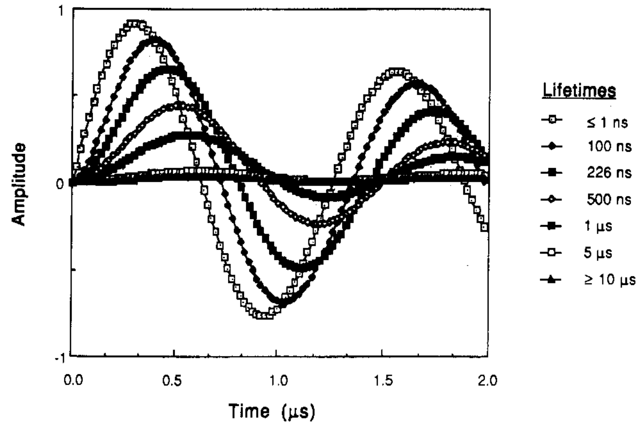

Figure 7. Photoacoustic signal amplitudes based on eq 1 for different transient lifetimes and with τ_0 = 3.5 μs and ν = 5 MHz. Lifetimes in microseconds from left to right (decreasing amplitude) are $\leq 10^{-3}$, 0.100, 0.226, 0.500, 1.00, 5.00, and ≥10.

of electronically excited $Cr(phen)_3^{3+}$. Each resulting waveform can be modeled as a damped harmonic oscillator. Because of the short relaxation time of the transducer, 3.5 μs, many additional waveforms are observed and cleanly resolved by the transducer (Figures 4 and 5). The additional waveforms are the result of acoustic reflections from the cuvette wall. The arrows in Figures 4–6 point to the waveform resulting from the initial, unreflected acoustic wave. All quantitative measurements were determined relative to the peak maximum of this waveform; the signal amplitudes shown are not normalized to sample absorbance. Figure 5 shows the response of the transducer to the initial and first reflected acoustic waves. Figure 6 shows the signal maxima and minima of $Cr(phen)_3^{3+}$ and $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ resulting from the initial acoustic wave. It is observed that the peak maxima of $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}Me_2phen)_3^{3+}$ (not shown) are slightly phase-shifted relative to $Cr(phen)_3^{3+}$.

Numerical Simulation of Transducer Response. Previous workers[12] have indicated that metastable excited states with lifetimes much greater than the frequency response of the transducer are needed in order to determine Φ_{isc}. Numerical modeling based on eq 1, shown in Figure 7, indicates that these metastable "product" excited states need have lifetimes only about 10 times the reciprocal of the frequency response of the transducer in order to obtain meaningful values of Φ_{isc}. This modeling further indicates that "precursor" transients with τ < 1 ns generate acoustic waves that appear as impulse δ functions to the transducer and are not time-resolved. Any product transients with τ > 5 μs cannot contribute significantly to the signal amplitude and are ignored. It is for these reasons that eq 1 can be reduced to eq 2. However, transients with 1 ns < τ < 5 μs generate acoustic waves that are time-resolved by the transucer, and each such transient gives rise to a unique waveform. These time-profile responses would be different for a transducer with a different resonant frequency. For example, a 50-MHz transducer would effectively ignore acoustic waves generated from transients with τ > 1 μs.

Intersystem Crossing Yields. Values of Φ_{isc} found for $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, and $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$ were 0.93 (±0.08), 0.95 (±0.03), and 1.04 (±0.05), respectively (5–10 determinations each). These values are in excellent agreement with the literature values of 0.95 (phen)[7] and 1.0 (bpy and phen)[8,9] reported for the first two of these complexes. Significantly larger values were found for $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}Me_2phen)_3^{3+}$, while a smaller value was found for $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$. These quantities and other pertinent information are summarized in Table I.

Our observations on $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ indicate that all upper excited states of these complexes decay promptly, $\tau <$ 15 ns (limited by laser pulse width), and efficiently (no measurable upper-state relaxation to the ground state) to populate the $^2T/^2E$ manifold. This behavior contrasts to that of $Cr(5\text{-}phen)_3^{3+}$, where a much larger percentage (27%) of the upper excited states relax promptly to the ground state. The prompt nonradiative pathways that populate the ground state compete well with intersystem crossing pathways and may result from spin–orbit coupling of the chlorinated ligand.

Our observations on $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}phen)_3^{3+}$ were somewhat surprising since use of eq 3 would give nominal values of $\Phi_{isc} = 1.19$ (±0.07) and 1.11 (±0.04), respectively. This strongly suggests that slow upper-state relaxation processes (>15 ns) or the formation of high-energy chemical products intervene for these complexes. Thus, in the limiting case of $Cr(NN)_3^{3+}$ complexes where all upper-excited-state processes have prompt nonradiative relaxation, we have $\Phi_{fl} \cong 0$ and $\Phi_{isc} = 1$. Then, on the basis of eq 2, the lowest excited state, ^2E, has a minimum $\eta_{pnr(lit.)}$ of $\eta_{pnr(lit.,min)} = 1 - (1)E_s/h\nu_{ex}$. For any system that has $\Phi_{isc} < 1$, $\eta_{pnr(lit.,min)} < \eta_{pnr(exptl)}$. However, for the above two complexes, $\eta_{pnr(lit.,min)} > \eta_{pnr(exptl)}$, which, on the basis of the time-profile response of the 5-MHz transducer (eq 1 and Figure 7), can only occur if there are additional upper-excited-state processes occurring that have lifetimes greater than 15 ns (i.e. energy is trapped in the upper excited states or high-energy intermediates). Under such circumstances, eq 1 cannot be reduced to eq 2, since the observed photoacoustic waveform is the sum of the waveform contributions from each of the upper-excited-state decays:[14]

$$V_t = \sum_{k=1}^{n} K''E_{abs}\eta_{nrk}\frac{\upsilon/\tau_k}{\upsilon^2 + (1/\tau_k')^2} \times \left\{e^{-t/\tau_k} - e^{-t/\tau_0}\left[\cos(\upsilon t) - \frac{1}{\upsilon\tau_k'}\sin(\upsilon t)\right]\right\} \quad (4)$$

where each waveform is weighted by an amplitude factor η_{nrk}, which represents the efficiency of the nonradiative process in emitting heat from transient k, K'' is a constant, and τ_k is the lifetime of transient k. The waveforms generated from $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and $Cr(4,7\text{-}Me_2phen)_3^{3+}$ had peak maxima that were shifted slightly toward longer time than the maxima of a standard waveform generated from prompt nonradiative decay (Figure 6).

Discussion

It is generally believed that back intersystem crossing from $^2T/^2E$ to $^4T_2$ is insignificant for $Cr(NN)_3^{3+}$ complexes.[1,6] If any of the upper excited states were to relax to the ground state or produce low-energy products, then $\Phi_{isc} < 1$. If any of the upper excited states had lifetimes that were longer than about 10 ns or if any of these upper states produced high-energy products, then Φ_{isc} based on eq 3 would be greater than 1.0. The results of our pulsed photoacoustic studies on these complexes span the full range of behavior.

Pulsed photoacoustic microcalorimetry is a powerful technique that can be used to probe the behavior of excited states or transients. It offers the advantage that it measures directly the nonradiative processes involved in relaxation of excited states. As a result, no approximations or assumptions of the pathways involved in relaxation of the excited state are needed as is typically the case with other kinds of measurements. We have used this technique to determine Φ_{isc} for several $Cr(NN)_3^{3+}$ complexes, where the results for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ agree nicely with the literature values and indicate that light absorption by these substrates leads to nearly 100% production of long-lived doublet states. Competing upper-state processes appear to intervene for certain substituted phenanthroline complexes. The small errors encountered with this technique are primarily the result of uncertainties in the $\eta_{pnr(lit.)}$ values calculated by using literature values of Φ_{fl} and average fluorescent frequencies.

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Registry No. bis-msb, 13280-61-0; $Cr(bpy)_3^{3+}$, 15276-15-0; $Cr(phen)_3^{3+}$, 15276-16-1; $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$, 51194-62-8; $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, 58220-56-7; $Cr(4,7\text{-}Ph_2phen)_3^{3+}$, 69178-81-0; $Cr(4,7\text{-}Me_2phen)_3^{3+}$, 51194-72-0; ethanol, 64-17-5; anthracene, 120-12-7; Rhodamine 6G, 989-38-8; fluorenone, 486-25-9; xanthone, 90-47-1.