Phosphorescence Lifetimes of $[Cr(NCS)_6]^{-3}$ in Frozen Alcohol Solvents

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For $[Cr(NCS)_6]^{-3}$ in normal alcohols at 77 K the lifetimes of phosphorescence from the excited doublet state are reported. The lifetimes decrease in the order ethanol > methanol > n-propanol > n-butanol > n-pentanol > n-hexanol > n-heptanol, and the rate constant increases exponentially when the 0′–0 band energy of the $^2E_g \rightarrow {}^4A_{2g}$ transition decreases.

Introduction

Though extensive studies of the solvent effect on the phosphorescence quenching in Cr III complexes have been carried out [1], our knowledge of the interactions leading to the radiationless relaxation is still insufficient.

In this paper we present the results of lifetime measurements of the phosphorescence of $[Cr(NCS)_6]^{-3}$ in frozen alcohol solvents. These results are correlated with measurements of the O′ – O phosphorescence transition. An interpretation of the data based on the classical energy gap law [2] is given.

Experimental

Materials

$(NH_4)_3[Cr(NCS)_6]$ was prepared as described in [3]. The commercially available (POCH Gliwice) alcohols were further purified following the literature procedures: methanol and n-propanol – refluxed over $Mg + I_2$ and distillated, ethanol – distillated after addition of Na, n-butanol, n-pentanol, n-hexanol and n-heptanol – addition of anhydrous K_2CO_3 and distillated.

Apparatus

Absorption spectra were recorded on a Cary 14 spectrophotometer. Phosphorescence spectra were measured on the spectrofluorometer constructed in our laboratory [4]. The phosphorescence beam was passed through a RG 2 glass filter, chopped and focused onto the entrance slit of a GDM 1000 monochromator (Carl Zeiss, Jena). The samples were frozen in a cylindrical cel in a Dewar-flask with liquid nitrogen. A mercury HBO 200 lamp with $CuSO_4$ solution and BG 18 glass filters was used as an excitation source. Luminescence decay times were measured at 77 K on a TRW Decay Time Fluorometer. A dye laser excited by a N_2 laser was used as an excitation source. Signals were observed on a 556 dual beam Tektronix oscilloscope.

Results

The peak wavelengths of absorption and phosphorescence spectra are given in Table 1. It is observed that the absorption and phosphorescence spectra shift to the red with increasing number of carbon atoms in the aliphatic chain of the alcohol. The total red shift of the absorption peak from ethanol and heptanol is about 410 cm^{-1} for $^4A_{2g} \rightarrow {}^4T_{2g}$ absorption and about 180 cm^{-1} for the phosphorescence $^2E_g \rightarrow {}^4A_{2g}$ O′ – O transition. The O′ – O transition was supposed to be identical with the maximum peak basing on the earlier analysis of phosphorescence spectra of $K_3[Cr(NCS)_6]$ carried out by Flint [5]. The phosphorescence lifetimes at liquid nitrogen temperature are listed in Table 1. It is seen that the lifetime decreases in the order
ethanol > methanol > n-propanol > n-butanol
> n-pentanol > n-hexanol > n-heptanol.

Discussion

It is easily seen from the absorption spectra that the oscillator strenghts of the allowed transition

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Solvent	Decay time at 77 K	Absorption		Emission $^2E_g \rightarrow {}^4A_{2g}$
		$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}$	
	[ms]	[cm^{-1}]	[cm^{-1}]	[cm^{-1}]
1 methanol	6.9	17795	24155	12890
2 ethanol	7.7	18050	24270	12880
3 n-propanol	7.0	17730	24040	12865
4 n-butanol	5.2	17730	23980	12790
5 n-pentanol	4.2	17700	23940	12765
6 n-hexanol	2.5	17670	23920	12740
7 n-heptanol	2.0	17640	23810	12700

Table 1. Absorption and emission peak position and decay time of $[Cr(NCS)_6]^{-3}$ ion in alcohols.

$^4A_{2g} \rightarrow {}^4T_{2g}$ are not influenced noticeably by the solvent. It may be simply exemplified by comparing the absorption bands of $[Cr(NCS)_6]^{-3}$ for the two alcohols exhibiting the largest lifetime differences, i. e. ethanol and hexanol (see Figure 1). The oscillator strenghts for ethanol and heptanol are practically the same, $f = 2.04 \cdot 10^{3}$. This means that the decrease of the phosphorescence lifetime should be attributed to the enhancement of the nonradiative decay path of the excited doublet state.

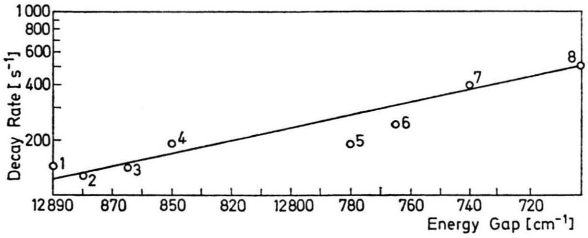

Fig. 2. The dependence of decay rate on the energy gap.

The interaction between the $[Cr(NCS)_6]^{-3}$ complex ion and alcohols is weak as can be seen from the phosphorescence spectra being not strongly modified by the alcohol solvents [6]. Only the peak positions of the O′ – O transition and the vibronic band shift gradually to the red. This leads naturally to a modification of the Franck-Condon factors. Assuming that the microscopic parameters, except the energy distance ΔE of the O′ – O transition, appearing in the Franck-Condon factor remain unperturbated by the solvents we may try to correlate the lifetime variation to the energy distance shift. In Fig. 2 we have plotted the dependence of the decay rates on the energy gas ΔE. A good linearity in the logarithmic scale is observed, which suggests a relation $\tau = A \exp(\alpha \Delta E)$, where α and A are independent of ΔE. This relation may be well rationalized within the framework of the theory of radiationless transitions in the weak coupling limit [2], which predicts the exponential dependence of the rate constant on the energy gap. One question remains to answer: Why does methanol exhibit an unusual behaviour?

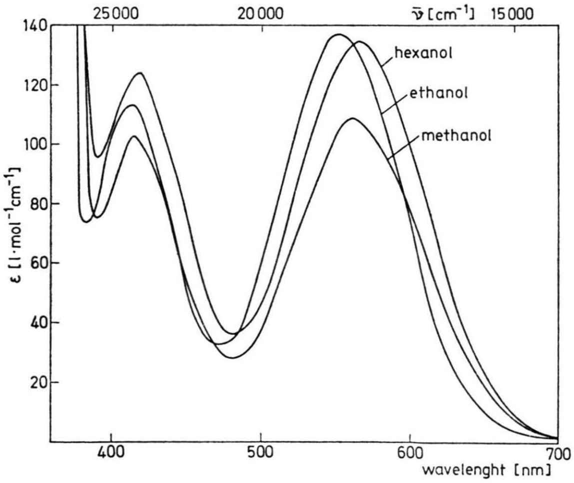

Fig. 1. Absorption spectra of $[Cr(NCS)_6]^{-3}$ ion dissolved in methanol, ethanol and hexanol.

In our opinion the exceptional behaviour of $[Cr(NCS)_6]^{-3}$ in methanol may be attributed to hydrogen bonding. The hydrogen bond strenght in methanol is stronger than in other alcohols for which it remains practically constant [7]. This interpretation is consistent with recent results of Cramer and Spears [8], who have reported a strong correlation between hydrogen bonding and nonradiative transitions in solute molecules.

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[1] E. Zinato, in Concepts of Inorganic Photochemistry, A. W. Adamson and P. F. Fleischauer, Eds., Wiley, New York 1975. A. W. Adamson and A. R. Gutieriez, J. Phys. Chem. **82**, 902 (1978); Y. Sik Kang, F. Castelli, and L. S. Forster, J. Phys. Chem. **83**, 2368 (1979). A. T. Walters and A. W. Adamson, Acta Chem. Scand. **A33**, 53 (1979).

[2] R. Englman and J. Jortner, Mol. Phys. **18**, 145 (1970).

[3] G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 2, Academic Press, New York 1963.

[4] W. Stręk, E. Łukowiak, and B. Jeżowska-Trzebiatowska, J. Lumin. **15**, 437 (1977).

[5] C. D. Flint and A. P. Matthews, J. Chem. Soc. Faraday Trans. II, **70**, 1301 (1974).

[6] to be published.

[7] M. D. Joesten and L. J. Schaad, Hydrogen Bonding, Dekker, New York 1974.

[8] L. E. Cramer and K. G. Spears, J. Amer. Chem. Soc. **100**, 221 (1978).