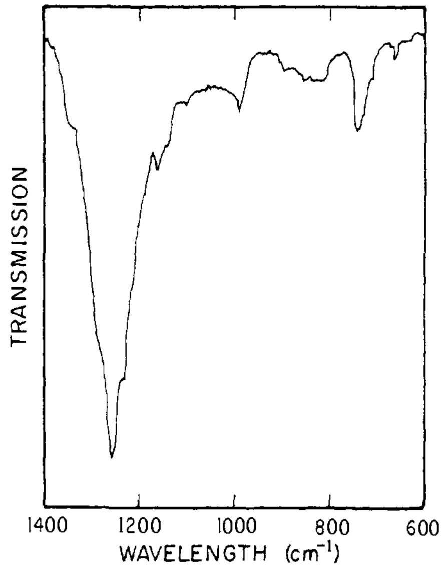

Figure 1.

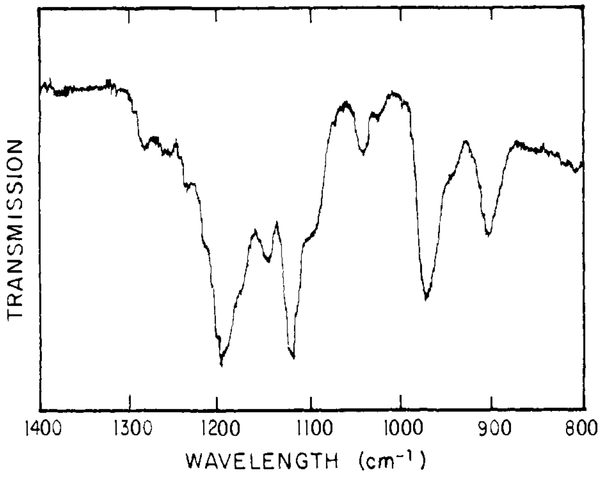

Figure 2.

tain the spectrum in Figure 2 which has a number of similarities to the spectrum of $Hg(CF_3)_2$. A complete vibrational analysis has not yet been possible because decomposition occurs with a Raman laser source.

Electron impact mass spectra of the $Xe(CF_3)_2$ showed peaks for Xe^+, Xe^{2+}, CF_3^+, and $C_2F_5^+$. Samples of the compound introduced through a 150 °C heated inlet gave Xe^+, Xe^{2+}, and a large number of fluorocarbon peaks ranging as high as *m/e* 498. Chemical ionization mass spectra of the compound using methane gas gave peaks representing Xe^+, CF_3^+, $C_2F_5^+$, XeF^+, XeF_2H^+, and a small amount of $C_2F_4^+$. Samples which had been stored at liquid nitrogen temperatures for several days showed, in addition, peaks representing $C_2F_4H^+$ and $C_3F_8H^+$. The ions XeF^+ and XeF_2H^+ are also observed in the chemical ionization mass spectra of XeF_2, but in this case the XeF^+/XeF_2H^+ ratio is 10, while that ratio is 1.6 for the $Xe(CF_3)_2$ compound. This result is consistent with the thermal decomposition of $Xe(CF_3)_2$ to XeF_2. Isobutane was unsuccessful in producing a chemical ionization spectra.

Acquisition of ^{19}F NMR evidence has been greatly hampered by lack of a suitable solvent. Although over 20 solvents have been considered, two categories have been observed: those in which decomposition occurs rapidly, and those (mostly fluorocarbons) in which the new fluorocarbon material is insoluble. In methylene chloride the compound decomposes rapidly to give xenon difluoride and fluorocarbons. A Fourier transform ^{19}F spectrum was obtained very rapidly during the process of decomposition in methylene chloride at −85 °C in FEP tubing. This ^{19}F NMR spectrum shows a peak at δ −9.6 ppm relative to $CFCl_3$ with two side bands indicative of the xenon-129 isotope (spin = $^1/_2$, 26.44% natural abundance). The ^{19}F-^{129}Xe two-bond coupling constant observed for this is 1940 Hz. This is smaller than the one-bond coupling of 5550 Hz in XeF_2[6] and larger than the three-bond coupling of 18 Hz in $FXeN(SO_2F)_2$.[2]

Confirmation of these observations awaits ^{19}F and ^{13}C or ^{129}Xe spectra in a suitable solvent.

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Evidence of Vibronic State "Selectivity" in the Photoracemization of Tris(1,10-phenanthroline)chromium(III) Ion in Solution

Sir:

Photoracemization of (+)-tris(1,10-phenanthroline)chromium(III) ((+)-$Cr(phen)_3{}^{3+}$) has been observed to be partially quenched by I^- and O_2, but there is a residual nonquenchable limit which was assigned to immediate reaction from the initially excited ^4T state (approximate octahedral microsymmetry) preceding intersystem crossing to the quenchable ^2E state.[1] Subsequently, it has become clear that intersystem crossing from ^4T states in Cr(III) complexes is a fast (picosecond) process[2,3] and that intersystem crossing shows wavelength dependence indicating a common time scale for intersystem crossing and vibrational relaxation.[3,4] If there is a fraction of reaction which proceeds from the quartet prior to intersystem crossing, this reactivity might be expected to occur in competition with vibrational relaxation, i.e. to display vibronic state selectivity. This point can be tested by examining wavelength dependence at high quencher concentrations where only the direct quartet reaction is observed.

First-order plots of decay of optical activity of (+)-$Cr(phen)_3Cl_3$ were obtained for irradiation at argon ion laser wavelengths of 457.9, 465.8, 488.0, and 514.5 nm. Data quality and precision is illustrated by the runs presented in Figure 1. The experimental procedure included the following features: (i) (+)-$Cr(phen)_3{}^{3+}$ solutions were prepared gravimetrically

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Table I

λ, nm	[(+)-Cr(phen)$_3$$^{+3}$], (mol dm^{-3} × 10^3)	intensity,[a] einsteins s^{-1} × 10^7	pH	*T*, °C	quantum yields, % $\phi_{rac}(N_2)$[b]	ϕ_{rac}(CsI) × 1
514.5	2.05	1.050	5.8	20	0.0177 ± 0.0012[e]	1.73 ± 13[e]
488.0	1.49	0.995	5.8	20	0.0299 ± 0.0015	2.04 ± 12
465.8	1.14	0.471	5.8	20	0.0292 ± 0.0015	2.10 ± 12
457.9	0.75	4.310	5.8	20	0.0353 ± 0.0018	2.79 ± 11
457.9	1.31	2.730	5.9	20	0.0372 ± 0.0019	2.62 ± 10
457.9	2.38	4.540	6.0	90	0.0316 ± 0.0022	2.86 ± 10
514.5[d]	2.74	0.896	5.8	25	0.0160 ± 0.0012	0.9 ± 15
488.0[d]	2.74	2.490	5.8	25	0.0270 ± 0.0018	1.4 ± 15
514.5	1.19	1.736	3.0	20	0.0327 ± 0.0016	2.64 ± 25
488.0	0.56	5.136	3.0	20	0.0367 ± 0.0018	4.09 ± 12

[a] Measured using reineckate actinometry. [b] Solution purged with doubly scrubbed $N_2(CrSO_4{\cdot}5H_2O)$ to zero $^2E \rightarrow {}^4A$ quenching. [c] [CsI] $\simeq 3.2 \times 10^{-3}$ mol dm^{-3}, i.e., a concentration of I$^-$ ion above that required to quench $^2E \rightarrow {}^4A$ phosphorescence by >99% (ref 1). [d] [CsI]-saturated solution with extensive I$^-$ ion association presumably present. [e] Error estimates are maximum spread of reported runs and *not* average or standard deviations.

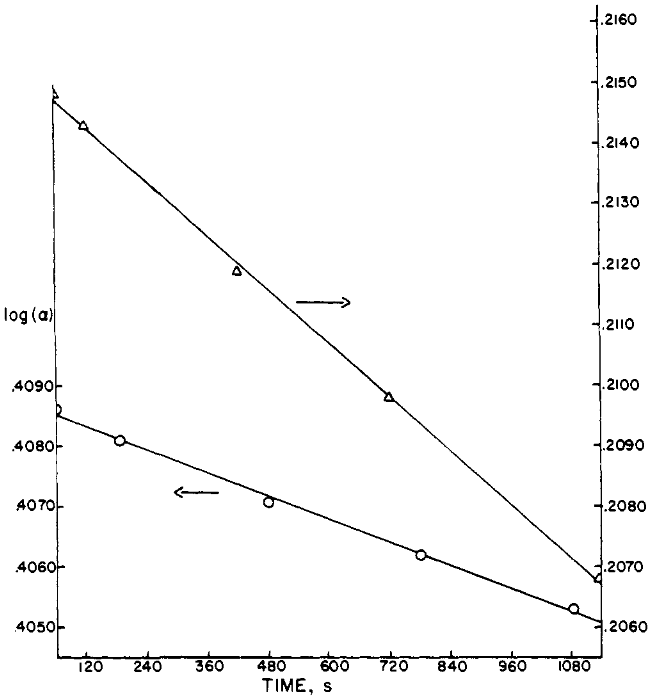

Figure 1. First-order rate plots for photoracemization reactions: upper curve for 488-nm irradiation with intensity of 9.95 × 10^{-8} einstein s^{-1} of a solution of 1.49 × 10^{-3} mol dm^{-3} complex at pH 5.8 (*T* = 20 °C with a percent adsorption of 64.7 and [CsI] = 3.12 × 10^{-3} mol dm^{-3}); lower curve for 514-nm irradiation with intensity of 1.05 × 10^{-7} einstein s^{-1} of a solution of 2.05 × 10^{-3} mol dm^{-3} complex at pH 5.8 (*T* = 20 °C with percent adsorption of 43.1 and [CsI] = 3.25 × 10^{-3} mol dm^{-3}).

just prior to use; (ii) solutions were filtered through 0.45-μ millipore filters, pH was recorded, and absorbance (hence concentrations also) was checked using a Cary 14 equipped with a 0.2-Å slidewire; (iii) solutions were divided into three portions and treated with either air, purified N_2, or CsI and then immediately photolyzed in 10.00-cm polarimeter cells; (iv) rotations were monitored to ±0.001° with a Perkin-Elmer Model 141 automatic polarimeter; (v) parallel thermal runs confirmed negligible thermal corrections. As has been pointed out before,[1] the first-order plots for photoracemization processes where an automatic correction enters for "product absorption" and where secondary photolysis problems can be minimized provide an opportunity for unusually high precision in quantum yield measurements. It is the obvious case for hunting the subtle variations sought here.

These reactions were found to show some dependence on ionic strength, pH, temperature, and even (weakly) complex concentration. Results are collected in Table I for a variety of conditions. These results *consistently show a wavelength dependence* in the nonquenchable fraction. To ensure that no feature unique to I$^-$ quenching is involved, we confirmed that O_2 quenching of the reaction precisely parallels I$^-$ quenching. Therefore, *quantum yields for racemization increase somewhat with increasing initial vibronic excitation* across the low energy side of the first quartet band. (Of course, a large effect is not expected.)

With this conclusion in hand for quenched reactions, it is interesting to return to the *similar* wavelength dependence observed for *nonquenched* reactions in N_2-purged solutions. This wavelength dependence no doubt reflects wavelength dependence of the intersystem crossing yield.[3,4] This dependence has been associated by earlier authors with the failure of the quartet, at lower levels of vibrational excitation, to efficiently intersect (and come into resonance with) vibronic components of doublets.[3,4] A parallel between intersystem crossing yield and "nonquenchable" quartet racemization yield is to be expected since both processes increase in efficiency with increasing vibronic excitation *until an upper limit is reached.* The earlier reports indicating a change in intersystem crossing yields with excitation wavelength do not indicate large changes in this parameter in wavelength ranges comparable with that explored here. This may be attributed to the fact that a significant intersystem crossing contribution does arise from the vibrationally equilibrated quartet. In our case, contribution to nonquenchable reaction from the vibrationally equilibrated quartet would limit the wavelength dependence of reaction yields to a narrow range. This is probably the case. The reaction is simply somewhat more efficient from higher vibronic levels. It is to be noted that reaction yields at 457.9 nm are in reasonable agreement with those measured earlier at 350 nm.[1]

A general observation is useful here. There are two limiting cases of photoreaction. The first is the photochemistry of vibrationally (thermally) equilibrated excited states where photochemistry is simply the study of the reactivity of an "electronic isomer" of the ground state; this is demonstrably appropriate for the near microsecond lifetime ^2E states of Cr(III) complexes and has been discussed in the context of structure reactivity relationships for the electron-transfer quenching of the ^2E of Cr(bipy)$_3$$^{3+}$.[6] The second limit is shown here. Reaction competes with vibrational deactivation. This limit might be usefully termed a *photophysical* limit.

Finally, it may be noted that this report does not contain the first report of complex wavelength dependence in quantum yields for reactions of Cr(III) complexes. The most detailed and precise study in the literature which is the one used for activometry[5] shows wavelength dependence which has not been fully analyzed.

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Ordered Structure in Dilute Solutions of Ionic Biopolymers. 1. Preliminary Small-Angle X-ray Scattering Study of Aqueous Solutions of Sodium Polyacrylate[1]

Sir:

In 1965[2] we measured directly for the first time the mean activity coefficient (γ) of a polyelectrolyte and found that

$$\log \gamma = a + bm^{1/3} \qquad (1)$$

a, b are constants and m is polyelectrolyte concentration was valid for a variety of synthetic polyelectrolytes. On the basis of the interpretation advanced by Frank and Thompson,[3] the cube-root dependence was taken as suggesting that a more or less regular lattice-like ionic distribution exists in the solutions as a result of intermacroion linkage through the intermediary of counterions. In addition to the well-known low intensity of scattered light from the salt-free polyelectrolyte solutions,[4] the following experimental supports for such an ordered structure have recently been documented: the catastrophic change of the diffusion coefficient with salt concentration observed by the dynamic light scattering[5] for poly-L-lysine and the presence of the peak in the scattered intensity of neutron beam at small angles for sodium polyacrylate.[6-7] In this report, we describe a new evidence obtained by small-angle X-ray scattering.

Polyacrylic acid (PAA) of Wako Chemical Co., Osaka, was carefully fractionated into nine fractions by using 1,4-dioxane and *n*-heptane as solvent and precipitant, respectively.[8] The fractionated sample was purified carefully by ion exchange and repeated precipitation and finally freeze dried. The degree of neutralization was adjusted by addition of a NaOH solution. The water for solution preparation was purified first by ion exchange and subsequently by distillation from a quartz vessel under nitrogen atmosphere, in order to remove ionic impurities, which were supposed to vitiate the ordered distribution. The X-ray source was a Rigaku RU-200A (60 kV, 200 mA) and the scattered intensity of the Cu Kα X-ray was measured by using a position-sensitive proportional counter. Refer to a previous publication for a detailed description.[9] All measurements were made with a point-focussing camera system. The solutions were put in a compartment between two parallel mica films (1 or 2 mm apart). The scattering intensities both from solution and solvent were corrected for their respective absorptions.

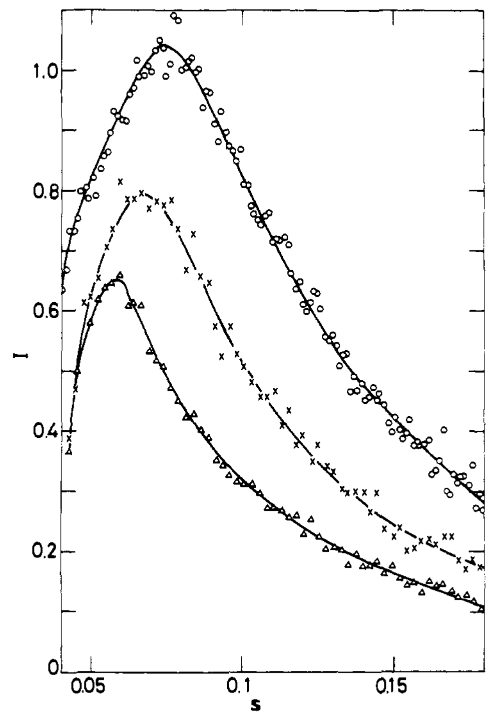

Figure 1. Scattered intensity vs. scattering vector plots for sodium polyacrylate solutions at 25 °C (weight-average degree of polymerization = 1020, degree of neutralization = 0.4): ○, 0.03 g/mL; ×, 0.02; △, 0.013.

Figure 1 shows the scattered intensity as a function of the scattering vectors **s** ($|\mathbf{s}| = 4\pi \sin \theta/\lambda$, where λ and 2θ are the wavelength of the X-ray used and the scattering angle, respectively) for a PAA sample ($\bar{P}w = 1020$) at three concentrations. It is clearly seen that the intensity I has a peak in the small angle region. The scattering peak was observed even at a low degree of neutralization, i.e., $\alpha = 0.1$, though the scattering curve is not given here. Although rather astonishing, this finding is consistent with the previously observed fact that the cube-root relation held also for polyions of a low charge density.[10] However, no peak was observed for polyacrylic acid at $\alpha = 0$.

When estimated by the Bragg relation ($2D_{\text{exp}} = 2\pi/\mathbf{s}_{\text{m}}$, where $\mathbf{s}_{\text{m}}$ is the **s** value at the peak), the dimension of the repeating unit of ordered structure ($2D_{\text{exp}}$) was fairly large (70–130 Å). It is most tempting to suggest that such a large distance is due to a regular distribution of the macroions. The next question is the mode of the distribution. Although the argument cannot be conclusive at present, there might be two asymmetric lattice structures for fully stretched rod-like macroions, namely the lattice proposed by Lifson and Katchalsky (L-K)[11] and hexagonal one.[12] The intermacroion distance calculated by the two models[13] was found to be smaller than, though fairly close to, $2D_{\text{exp}}$. This may suggest that the asymmetric lattice-like distribution is highly plausible. However, when the macroions are not fully extended as under our experimental condition, the hexagonal lattice dimensions would become larger. The computed minimum intermacroion distances for the symmetrical structures, i.e., simple cubic, body-centered cubic, and face-centered cubic, with the same density of macroions were much larger than $2D_{\text{exp}}$, suggesting that the symmetrical structures might be less important.

The decreasing tendency of $2D_{\text{exp}}$ with increasing concentration (c) at a fixed degree of neutralization (α) would be readily accepted. Further, $2D_{\text{exp}}$ was found to decrease with increasing α at a fixed c, which was surprising at a first glance, but might indicate that the ordered distribution is not due to "repulsion" between the macroions as claimed often,[4] but due

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