Vibrational Circular Dichroism of Dimethyl Tartrate. A Coupled Oscillator

Sir:

We have demonstrated that vibrational circular dichroism (VCD)—the differential absorption of left and right circularly polarized light by vibrational modes of chiral molecules—is a measurable phenomenon and is common to a wide variety of optically active compounds.[1] To date, interpretation of VCD data has been limited, partially owing to the complexity of theoretical treatments requiring a complete normal mode analysis.[2] However, for dimeric molecules, whose chirality is a result of the coupling of two equivalent monomers, a simple coupled oscillator theory (also refered to as degenerate coupled oscillator theory) is possible.[3] We have found that the OH stretching band of dimethyl tartrate yields VCD that appears to provide the first example of this coupled oscillator mechanism.

The VCD and absorption spectrum of the OH fundamental stretching band of dimethyl-*d* tartrate in dilute $\mathrm{CCl_4}$ solution are shown in Figure 1. The spectra were measured as described earlier,[1] but have been digitized and replotted. VCD and absorption spectra of this band are concentration dependent, but the spectra shown in Figure 1 are unaffected by further dilution.

The interaction of vibrational modes of equivalent monomers leads to two modes, symmetric (+) and antisymmetric (−), split by $2V$. Coupled oscillator theory predicts equal and opposite rotational strengths for these modes: $R_+ = -R_-$.[3] In the case for which $2V$ is much smaller than the absorption bandwidth, the VCD is predicted to have sigmoidal dispersion, its sign and magnitude depending on the signs and magnitudes of V and $R_\pm$. $R_\pm$ can be calculated from the electric dipole transition moment and the molecular geometry.

The VCD shown in Figure 1 exhibits this typical coupled oscillator dispersion and is the first example we have found of this phenomenon.

The calculation of the VCD of dimethyl tartrate requires, first, knowledge of the molecular structure and, second, calculation of V and $R_\pm$. We believe the most probable conformation of dimethyl tartrate in $\mathrm{CCl_4}$, at dilutions sufficient to make intermolecular hydrogen bonding negligible, to be the bicyclic structure shown in Figure 2. Each six-membered ring is formed by the internal hydrogen bonding of OH and $\mathrm{COOCH_3}$ groups from opposite halves of the molecule. This structure is consistent with the observed OH frequency, the small NMR coupling constant of the vicinal CH protons, the bond angles and lengths from known tartrate x-ray structures, and theoretical calculations of the minimum energy conformation.[4]

Using the dipole transition moment obtained from the absorption spectrum and this structure, we calculate $R_\pm = \pm 1.8 \times 10^{-43}$ (esu·cm)^2. Using this value and the observed absorption bandwidth, the experimental VCD is reproduced with $2V \simeq -3$ cm^{-1} (with asymmetric mode being higher in energy than symmetric mode). Assuming no other interactions, V can also be estimated using the dipole-dipole approximation of exciton theory, which yields a negative value of magnitude <0.6 cm^{-1}.

We find, therefore, that, with the assumed structure (Figure 2), the simple coupled oscillator model predicts VCD of the correct sign but of a magnitude appreciably smaller than observed. This theoretical inadequacy may derive either from the postulated structure or the use of the coupled oscillator theory on this molecule. We are currently pursuing more detailed theoretical calculations to elucidate this question.[2] To provide a more extensive basis for the evaluation of theoretical models we have also obtained VCD data for the OH, OD, CH, and CD stretching modes of dimethyl-d_0, -d_2, -d_6, and -d_8 tartrates which will be reported in a future publication.[4] We merely stress, in conclusion, that, if reliable theoretical calculations of VCD can be shown to be practicable, the measurement of VCD provides a method for the determination of absolute configuration and conformation of chiral molecules.

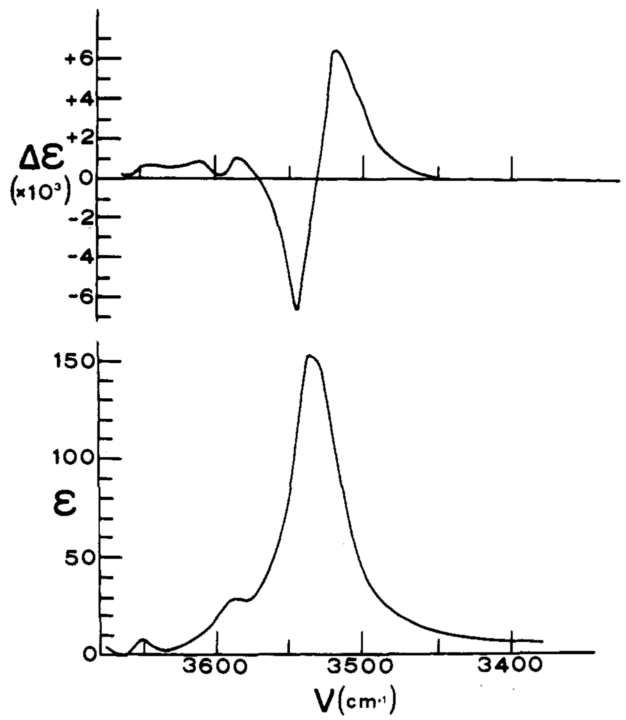

Figure 1. VCD and absorption spectra of dimethyl-*d* tartrate in $\mathrm{CCl_4}$ solution over the OH stretching region: 0.0122 M, 0.323-cm path. Spectra have been digitized and replotted in terms of ϵ and $\Delta\epsilon$ and have been converted to be linear in wavenumber. Random noise level of the VCD was $\Delta\epsilon \le 0.7 \times 10^{-3}$; base-line deviations were $\Delta\epsilon \le 1.5 \times 10^{-3}$.

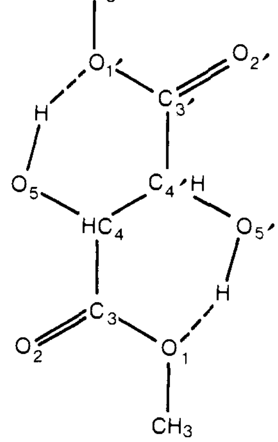

Figure 2. Projection of the proposed dimethyl tartrate structure on the *x*-*y* plane. Assumed internal hydrogen bonds are indicated by dashed lines. The alternate structure with hydrogen bonds to O_2 and $O_{2'}$ leads to the same interpretation.

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References and Notes

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(2) J. A. Schellman, *J. Chem. Phys.*, **58**, 2882 (1973); **60**, 343 (1974).

(3) See, for example, G. Holzwarth and I. Chabay, *J. Chem. Phys.*, **57**, 1632

(1972); T. R. Faulkner, Ph.D. Thesis, University of Minnesota, 1976; and references.
(4) T. A. Keiderling and P. J. Stephens, unpublished work.

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Triplet–Triplet Annihilation of $Ru(bpy)_3^{2+}$ in Micelle Solutions

Sir:

Considerable attention has been paid in the past few years to photochemical and radiation-chemical reactions in micellar systems.[1-5] In the present work solutions of ruthenium tris-(2,2′-bipyridyl) [$Ru(bpy)_3^{2+}$] in negatively charged sodium dodecyl sulfate (SDS) micelles[6] are submitted to pulsed N_2 laser excitation. The purpose of the study is to show that the nonhomogeneous distribution of excited triplet states of molecules incorporated in micelles may be used for markedly enhancing the efficiency of triplet–triplet annihilation.

Experiments were first carried out exposing 10^{-4} M deaerated (SDS free) aqueous solutions of $Ru(bpy)_3^{2+}$ to the exciting (8 ns, 337.1 nm, 0.5 mJ) pulses in an N_2 laser photolysis system.[7] The solutions were found to exhibit transient absorbance changes identical with those previously reported by Bensasson et al.[8] following excitation by a 530-nm neodymium laser pulse. The depletion of the ground-state absorbance ~450 nm and the increase in absorbance ~360 nm are due to the population of a triplet charge-transfer state of the metal complex.[8]

The triplet decay, back to the original ground-state ion, may be followed by monitoring the 610-nm phosphorescence, the triplet absorbance decay at 360 nm, or the ground-state regeneration at 450 nm. The process was found to be of first order with a lifetime ($\tau = 0.60 \pm 0.06$ μs) which is independent of the $Ru(bpy)_3^{2+}$ concentration (in the range 10^{-3}–10^{-5} M) and of the pulse intensity (in the range ~50–5 mJ/cm^2). This independence indicates the lack of any substantial triplet quenching effects, either by the ground state or, even under the maximum concentrations and excitation intensities available, by triplet–triplet annihilation.

Above 500 nm a small positive increase in absorbance which is markedly reduced in the presence of N_2O (1 atm) and 0.1 M *tert*-butyl alcohol, is attributed to the low-yield generation of solvated electrons, in keeping with the conclusions of Meisel et al.[9]

Experiments were subsequently carried out with $Ru(bpy)_3^{2+}$ solubilized in SDS micelles. Although the transient absorption spectra following laser excitation are identical with those observed in the micelle-free homogeneous aqueous solutions, the decay kinetics of the triplet state are markedly different. A relatively fast nonexponential process is now followed by a slow exponential decay characterized by a lifetime of $\tau = 0.80 \pm 0.08$ μs.

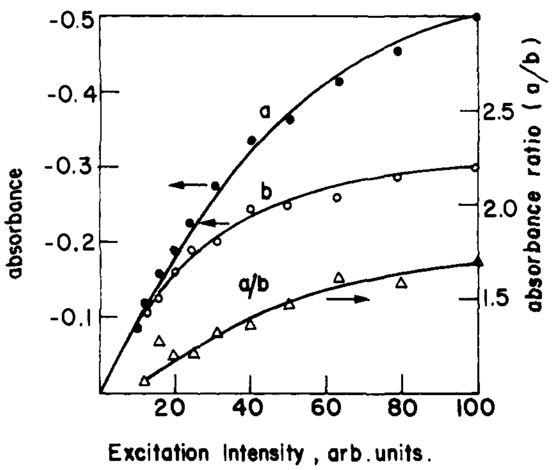

Figure 1. Laser intensity dependence of the amplitudes of the fast and slow triplet decay processes in a solution of 0.98 10^{-4} M $Ru(bpy)_3^{2+}$ and 1.0 10^{-2} M SDS. The amplitudes are monitored by the corresponding decrease in absorbance (bleaching) at 450 nm. (a) The initial bleaching at zero time. (b) Value obtained by extrapolation of the slow decay component to zero time. (a/b) The ratio between the former values. (Full intensity scale is equivalent to ~50 mJ/cm^2.)

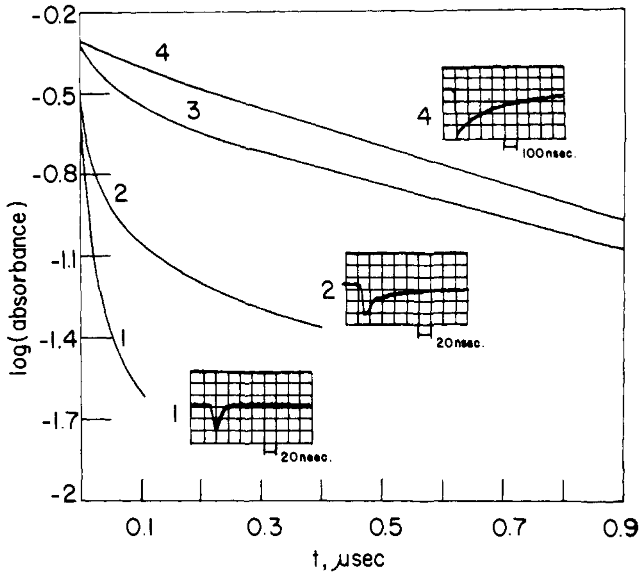

Figure 2. Characteristic oscillograms (upper trace monitoring light off, lower trace monitoring light on) of the bleaching at 450 nm and corresponding absorbance decay curves, showing the effects of varying the SDS concentration at a constant pulse intensity (~50 mJ/cm^2) on the decay of the triplet state in 1.0 10^{-4} M $Ru(bpy)_3^{2+}$ solutions. SDS concentrations are (1) 3.1 10^{-3} M, (2) 6.3 10^{-3} M, (3) 1.3 10^{-2} M, (4) 3.2 10^{-2} M.

The initial amount of bleaching and the triplet decay kinetics were measured at 450 nm as functions of the intensity of the exciting pulse. The rate of the slow decay process was found to be independent of the excitation intensity. For each intensity value the decay curve corresponding to this process was plotted on a logarithmic scale and extrapolated to zero time. Figure 1 shows the initial amount of bleaching (a) and the initial extrapolated component (b), both as functions of the excitation intensity. The intensity dependence of the absorbance ratio (a/b) shown in Figure 1 clearly indicates that the two decays cannot be represented by two consecutive first-order processes. The observed relationship strongly suggests that the initial component is due to a fast bimolecular triplet–triplet annihilation reaction.

To further confirm this conclusion and also to discriminate between inter- and intramicellar annihilation reactions, relatively high-intensity experiments were carried out in solutions with varying micelle concentrations in the presence of a constant amount of $Ru(bpy)_3^{2+}$. The observations are summarized in Figure 2. At very low micelle concentrations (i.e., when the number of $Ru(bpy)_3^{2+}$ ions per micelle is high) the lifetime of fast component is so fast ($\tau < 5$ ns) as to essentially follow the laser pulse profile. Under such conditions the amplitude (b) of the slow decay is negligible. When the micelle concentration increases and, consequently, there are less $Ru(bpy)_3^{2+}$ ions per micelle, the lifetime of the fast decay increases and its