greater extent at the transition state than have changes in covalent bonding. This qualitative conclusion is in agreement with proposals[2,12] that the activation process for solvolysis in water is primarily a reorganization of solvent structure. Furthermore, the value of $pK_a(\ddagger)$ itself falls in the range which has been shown for some other hydrolyses[2] to be consistent with the absence of any nucleophile-carbon covalent bonding in the transition state.

In summary, this work demonstrates the feasibility of measuring $\Delta C_p°(\ddagger)$ values and suggests that they (in combination with values of $\Delta S°(\ddagger)$) may be particularly valuable in characterizing the structure of the solvent in the transition state. However, interpretations of these values which are more quantitative than those included here should await the accumulation of a larger set of reliable $\Delta C_p°$ and $\Delta S°$ values than is presently available.[13]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

References and Notes

(1) To avoid confusion concerning the standard state for water, a molar standard state is used throughout this discussion. Thus pK_a (H_2O) = 15.74 at 25° and the pH-independent part of the hydrolysis rate must be written as in eq 1.[2]

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Vibrational Circular Dichroism of 2,2,2-Trifluoro-1-phenylethanol

Sir:

We report the observation of circular dichroism (CD) in vibrational bands of liquid (*S*)-(+)- and (*R*)-(−)-trifluoro-1-phenylethanol, $C_6H_5CH(OH)CF_3$ (I). The CD of the C*-H stretching band of this same molecule was previously reported by Holzwarth et al.[1] in the first and only prior publication of vibrational CD measurements in the liquid phase. As a result of higher instrumental sensitivity we are able to improve on the earlier work and observe CD over a wider spectral region with higher signal-to-noise ratio.

The CD measurements were performed on a previously described infrared instrument.[2] Extensive modifications were made to improve the medium infrared performance;[3] the most important include the substitution of an InSb detector and a ZnSe modulator,[4] and the insertion of a second ZnSe modulator after the sample which enables artefact CD signals to be greatly reduced.[5]

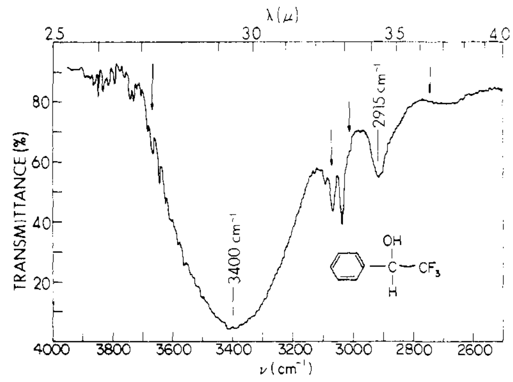

Figure 1. The transmission spectrum of liquid 2,2,2-trifluoro-1-phenylethanol with a spectral band pass of ~2 cm^{-1} and a pathlength of 20 μ. The wavelength limits of Figures 2 and 3 are indicated by arrows.

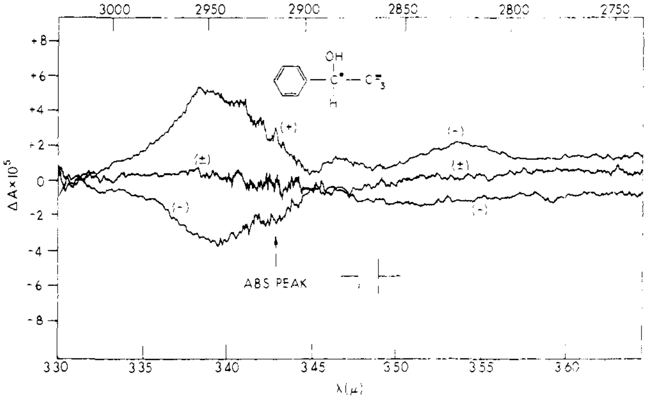

Figure 2. The CD spectrum of the C*-H stretching band of liquid 2,2,2-trifluoro-1-phenylethanol. $\Delta A = A_L - A_R$. The spectral band pass, shown in the figure, is 10 cm^{-1} and the time constant is 10 sec. The pathlength is 100 μ giving an absorbance *A* of 1.0 at the absorption peak, indicated by an arrow.

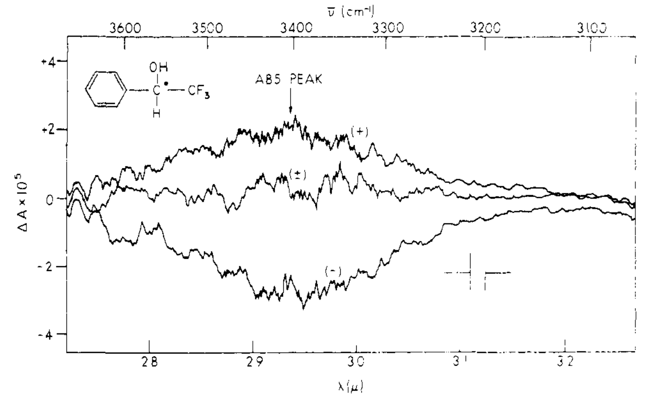

Figure 3. The CD spectrum of the O-H stretching band of liquid 2,2,2-trifluoro-1-phenylethanol. $\Delta A = A_L - A_R$. The spectral band pass, shown in the figure, is 15 cm^{-1} and the time constant is 10 sec. The pathlength is 20 μ giving an absorbance (*A*) of 1.0 at the absorption maximum, indicated by an arrow.

The liquid sample was held in a variable pathlength cell allowing adjustment to optimum absorbance settings. Both optical isomers and the racemic mixture of I were obtained commercially[6] and used without further purification.

Figure 1 shows the transmission spectrum of I. The O-H stretching motion is responsible for the broad 3400-cm^{-1} band; the sharp bands between 3100 and 3000 cm^{-1} are due to the phenyl C-H stretching vibrations, and the C*-H stretch is assigned to the 2915-cm^{-1} band.

Figure 2 shows the vibrational CD of the C*-H band. This consists of a principal component peaking ~30 cm^{-1}

higher than the absorption peak and a broader weaker tail. The ratio of the peak ΔA and peak A is 4.3×10^{-5}. The principal CD component was observed by Holzwarth et al. with much lower signal-to-noise ratio. The low energy tail was not observed.

Figure 3 shows the CD in the O-H stretching band. The sign is the same as in the C*-H band but the anisotropy ratio $\Delta A/A = 2.5 \times 10^{-5}$ is smaller by nearly a factor of 2. In this case the CD and absorption maxima correspond closely. No CD was reported in this band by Holzwarth et al.

The observation of vibrational CD with good signal-to-noise ratio in an unremarkable chiral molecule indicates that vibrational CD spectra should be generally observable with currently accessible instrumentation. Experiments are in progress to test this optimistic prognosis.

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The Effect of Ligand and Solvent Deuteration on the Excited State Properties of the Tris(2,2'-bipyridyl)ruthenium(II) Ion in Aqueous Solution. Evidence for Electron Transfer to Solvent

Sir:

Several recent studies have reported the use of $[Ru(bipy)_3]^{2+}$ to sensitize photoreactions in aqueous solution.[1-10] The quenching of the luminescence of this complex by other (presumably photoinert) molecules[11-16] has also been studied. Some authors postulate an electron transfer (photoredox) process involving excited state $[Ru(bipy)_3]^{2+}$ as a reducing agent[8-11] to explain the luminescence quenching, while others assume that a direct excitation energy transfer process occurs.[1-6,11-16] We wish to communicate observations of the luminescence lifetime and quantum yield of this ion in aqueous solution at 25°; conditions are typical of those employed in the references cited. In addition, the effect of deuteration of either the ligand, the solvent, or both, on the luminescence lifetime and quantum yield, was measured.

Commercial $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ (G. F. Smith Chemical Co.) was used without purification. The properties of this material were identical with those of samples which were synthesized and purified in this laboratory. The perdeuterated analog, $[Ru(bipy\text{-}d_8)_3]Cl_2 \cdot 6D_2O$, was prepared by the method of Burstall[17] using 60 mg of $RuCl_3 \cdot 3H_2O$ (Englehard Industries) and 176 mg of the deuterated ligand (Merck Sharp and Dohme of Canada, Ltd.) which was first purified by vacuum sublimation. The product of this synthesis was recrystallized from D_2O. The absorption and emission spectra of deuterated complex agreed with those of the parent complex.[18-20]

Table I. Measured Lifetimes, μsec (Quantum Yields)

Sample	$[Ru(bipy)_3]Cl_2$	$[Ru(bipy\text{-}d_8)_3]Cl_2$
Solvent,		
H_2O; 25°	0.58 ± 0.04[a] (0.042 ± 0.003)	0.69 ± 0.03 (0.047 ± 0.003)
D_2O; 25°	1.02 (0.070)	1.25 (0.079)
4:1 v/v EtOH:MeOH; 77°K	5.1 ± 0.1[b]	6.1 ± 0.1
	Free Ligand Lifetimes, sec	
	bipy-h_8	bipy-d_8
4:1, v/v EtOH:MeOH; 77°K	0.97	2.2

[a] References 8, 11, and 12 report values of 0.66, 0.60, and 0.65 μsec, respectively, under similar conditions. [b] Reference 27 reports a value of 5.21 μsec for this system.

Luminescence measurements were made on the complexes dissolved in H_2O (deionized and then distilled) or in D_2O (used as supplied by Thompson Packard Inc.). The solutions were deoxygenated with dried, chromous-scrubbed nitrogen. All solutions were prepared fresh daily.

Luminescence quantum yields were measured by a modified Parker Rees method.[21,22] Fluorescein, purified by the method of Orndorff and Hemmer,[23] was used as a standard with a yield of 0.90.[24] The samples were excited at 436 nm using a 1000-W Hanovia Hg-Xe lamp. The exciting light was filtered through 7 cm of $CuSO_4$ (150 g/l.), and the desired line was isolated with a Bausch and Lomb monochromator having a 250-mm focal length and a grating blazed at 300 nm. The bandpass was limited to 5 nm. The output of this monochromator was modulated with a PAR Model 181 chopper and stray light was filtered with two Corning 9-58, one Corning 0-52, and an Optics Technology 430 blue edge filter before entering the cuvet containing the sample. The samples were maintained at 25.0 ± 0.1° with a water-jacketed cuvet holder and a Forma Temp Model 2095-2 bath. The emissions were monitored with a Perkin-Elmer Model 98 monochromator and an RCA C31034A photomultiplier having a 128 spectral response. The output was amplified with a PAR Model 184 lock-in amplifier and fed into a RDK Model B161 strip-chart recorder. The system was calibrated with an NBS L-101 standard lamp to correct for variations in instrumental response with wavelength. Lifetimes were measured in the manner described previously,[25] using the cell holder and bath mentioned above and monitoring at 610 nm.

Measurements on a Cary Model 118C spectrophotometer indicated that *the absorbance of 10^{-7} M oxygen-free solutions of the complexes was about 20% less than in air-saturated solutions.* The decrease in absorbance upon deoxygenation was uniform throughout the visible-uv region, and the original spectrum could be regenerated by reaerating the solution. We know of no previous report of this effect in transition metal systems, although dissolved oxygen is known to enhance the intensity of $T_1 \leftarrow S_0$ absorptions of aromatic hydrocarbons.[26] This effect of dissolved oxygen requires an additional precaution in the quantum yield measurements; i.e., absorbances as well as emission intensities must be determined on oxygen-free solutions or the measured absorbance will be high, resulting in a measured quantum yield which is lower than the true value.

The results summarized in Table I show a remarkable effect. Deuteration of the free ligand causes the measured lifetimes, τ_m, to more than double, consistent with the theories developed for organic systems.[28,29] The effect of