

Conversions over Low Barriers. 4. Dimer/Monomer Dissociation in Formic Acid

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Abstract: We describe an attempt to measure the relaxation time for the gas-phase dissociation/association of dimeric formic acid. This is the prototype of a weak bidentate complex, based on two O-H-O bonds. At the lowest temperature and pressure at which NMR spectra were recordable, the relaxation time for the dimer-monomer equilibration proved to be less than the shortest NMR relaxation which could be detected with a 300-MHz unit, for the ¹H₂O exchange. As a consequence the experiments demonstrated that the *E*₀ for dissociation is no more than 12 kcal/(mol of dimer), and that at pressures below 10 torr, the dissociation follows second-order kinetics.

The hydrogen bond occupies a unique niche in the chemical literature.¹ More than four score years have passed since an intramolecular H bond was first proposed by Hantzsch for acetoacetic ester (1910); four years later it was followed by Pfeiffer's suggestion that in the dimers of aliphatic acids the carboxyl ends combine to form ring structures with two H bonds. That the lowest energy conformation of formic acid monomer was trans (due to a weak intramolecular H bond) was indicated in 1937 by a rotational analysis of its second OH harmonic band at 10 200 cm⁻¹.² Eventually it was recognized that the aliphatic acids exist in a large variety of conformations, separated by relatively low barriers, such that many of these isomers are in dynamic equilibrium at ambient temperatures.

While the structures, spectroscopy, and thermochemistry of the monomer/dimer reactions of organic acids have been thoroughly explored, the literature on the dynamics of their numerous conformational interconversions is singularly sparse, except for the treatment of proton shifts in two-well potentials.³ Currently there is a vigorous discussion among theorists and experimentalists of the relaxation time for the double-H-shift in the ring of the dimers.⁴ We found no reports of attempts to measure the relaxation time for the dissociation/association in formic acid, the simplest prototype of a double-dentate reaction. Our objective in undertaking the experiments described below was to determine whether with currently available NMR units, working at the extremes of their sensitivity, one could measure, or at least set a lower limit, the dissociation rate constant of the dimer.

The following is a brief summary of some pertinent information on formic acid. The trans isomer is more stable than the cis by 3.9 kcal mol⁻¹,⁵ as expected, the cis has the larger dipole moment (3.79 D vs. 1.42 D).⁶ Microwave spectra not only provided precise structural parameters but also indicated that the barrier to rotation about the C-OH bond is 13.8 kcal mol⁻¹.⁷ Normal mode analyses led to straightforward assignments of the fundamental vibrational frequencies.⁸

In the gas phase dimerization lowers the enthalpy by 14.1 ± 1.5 kcal/(mol of dimer) and the entropy by 36.0 eu.⁹ The cyclic structure of the dimer was determined by electron diffraction¹⁰ and the dimensions of the C₂O₄H₂ ring in substituted acetic acids by microwave spectroscopy.¹¹ We found no reports on the thermochemistry for the monomer/dimer equilibrium in solutions of formic acid. In the solid state, polymers in the form of extended chains characterize the structure,¹² similar to those found in solid HF.¹³ Infrared spectra of the neat liquid suggest that the predominant forms are chains,¹⁴ similar to the configuration observed in the solid state, in contrast to neat acetic acid, where the predominant species appear to be ring dimers.¹⁵ The proton NMR spectrum of 97% neat formic acid, at room temperature, shows two singlets, ¹H_C ≈ 8 ppm and ¹H_O ≈ 11.4 ppm,¹⁶ downfield from Me₄Si.

Experimental Section

Formic acid (minimum purity 95%) was obtained from a commercial source. To thoroughly dry it and all the solvents used in these experiments, their vapors were passed under vacuum, through a column of molecular sieve (type 4A, 1/16 in.). Solutions in CDCl₃ [*μ* = 1.15 D] and CD₂Cl₂ [*μ* = 1.48 D], both ≈ 2% by volume in 5-mm NMR tubes, were prepared under vacuum manipulation. A small amount of Me₄Si was added for an internal reference before the tubes were sealed. The proton resonances were recorded on a Bruker-WM300 spectrometer, pulsed Fourier transform mode, operating at 300.1 MHz. Generally up to 60 scans were accumulated with a relaxation delay of 15 s. The probe temperature control was described in our previous communication.¹⁷ All samples were allowed to equilibrate for about 15 min at each temperature prior to spectral acquisition.

Several early attempts to obtain gas-phase ¹H NMR spectra gave essentially featureless records. It appears that formic acid is strongly adsorbed onto the glass surfaces of the NMR tubes. To minimize adsorption the following procedure was developed. (i) NMR tubes (15 mm) were washed thoroughly and soaked in a mixture of chromic-sulfuric acid for a few hours. After being rinsed with distilled water, ethanol, and hexane they were dried in an oven; then the tubes were immersed in

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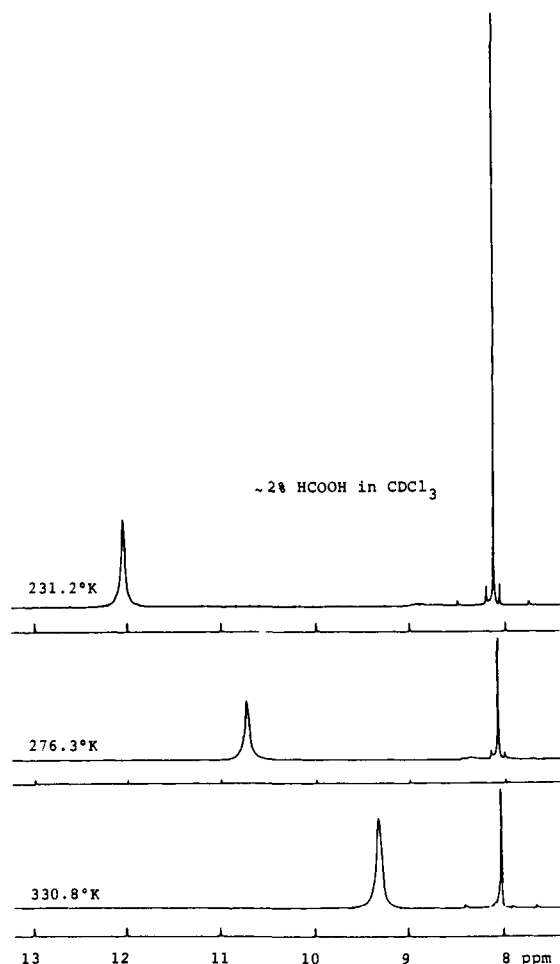


Figure 1. NMR spectra of dilute solutions (2%) of HCOOH in CDCl_3 .

trimethylchlorosilane (under reflux) for several days. They were washed with hexane and dried. (ii) Cylindrically symmetric vacuum valves for the 15-mm NMR tubes were constructed from KEL-F. These were unaffected by the chromic-sulfuric acid treatment. The NMR tubes were then evacuated and filled to the desired pressures (at 296 K) and sealed. With these precautions we were able to record useful NMR spectra.

The Bruker WM300 spectrometer was shimmed at each temperature until the best FID signal was obtained with a 15-mm NMR tube containing gaseous Me_4Si (400, 100, 30, and 11 torr). Routinely the resonance peak for the 400 torr sample had a fwhm of 1.5 Hz at room temperature. Over 60 000 transients were recorded for sample pressures as low as 2.5 torr with no relaxation delay time allowed due to a restriction on the allocated machine time. [We found no significant differences in line shapes between spectra recorded with long and without relaxation delay times for gaseous aziridine at $p = 28$ torr, and formic acid at 15 torr.]

Solution Studies

Proton resonances were recorded for dilute solutions in CDCl_3 over the temperature range 331–231 K and in CD_2Cl_2 for the range 309–240 K. At the lowest temperature sample inhomogeneities appeared, presumably due to phase separation of the solute. Typical spectra are shown in Figure 1. In both solvents the $^1\text{H}_\text{C}$ resonance was sharp and its position showed a very slight temperature dependence. In solutions of the trichlor it moved from 8.02 ppm at 330.8 K to 8.12 ppm at 231.2 K; in solutions of the dichlor it moved from 8.05 ppm at 308.7 K to 8.11 ppm at 240.4 K. The $^1\text{H}_\text{O}$ resonances are relatively broad; these moved appreciably toward lower fields when the temperature was lowered. In CDCl_3 solutions their fwhm was ≈ 15 Hz, and increased slightly with rising temperature, while the center position moved from 9.30 to 12.03 ppm; when CD_2Cl_2 was the solvent their fwhm was 25 ± 2 Hz and the corresponding linear shift was from 9.03 to 11.26 ppm, indicative of specific solvent effects (Table I). To account for these observations it is proposed that whatever factors are

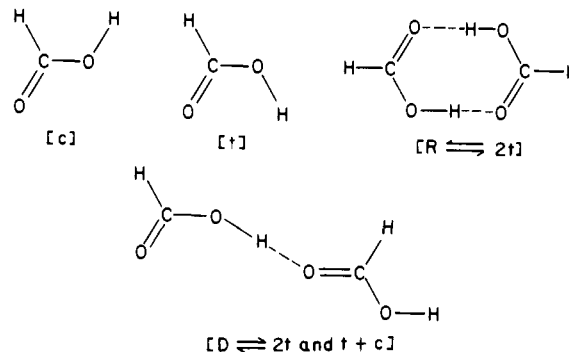
Table I. Observed Chemical Shifts for $\approx 2\%$ Solutions (HCOOH)

solvent	temp, K	$\delta_{^1\text{H}_\text{C}}$ (ppm)	$\delta_{^1\text{H}_\text{O}}$ (ppm)	K^c ^a
CDCl_3	330.8	8.02	9.30	1.296×10^{-3}
	296.2	8.05	10.15	2.724×10^{-4}
	276.3	8.07	10.72	9.902×10^{-5}
	253.7	8.09	11.46	1.870×10^{-5}
	231.2	8.12	12.03	1.493×10^{-6}
CD_2Cl_2	308.7	8.05	9.03	
	298.4	8.06	9.16	
	270.1	8.08	9.93	
	240.4	8.11	11.26	

^a $K^c \equiv 4a\alpha^2/(1-\alpha)$, where a is the total molar concentration as $(\text{HCOOH})_2$ and α is its degree of dissociation.

responsible for broad $^1\text{H}_\text{O}$ resonances, as they are in the alcohols (due to minute amounts of H_2O) broadening is additionally enhanced by the solvent dipoles; the larger the dipole moment of the surrounding molecule the greater the effect. These spectra give no indication of a rate-controlled process, nor is one expected for an unimolecular dissociation at the "high-pressure limit" with a dissociation energy of about 14 kcal mol⁻¹, unless a substantial barrier is present.

We propose that the shift of the $^1\text{H}_\text{O}$ resonances is due to changes in the monomer/dimer ratio. Since the chemical shifts for the structures (a few from the large number of possible configurations), are both temperature and solvent dependent, estimates



of an equilibrium constant can be made only after introducing several reasonable assumptions.

(i) In dilute solutions the concentration of the [D] structure is small, so that the dominant equilibrium involves $\text{R} \rightleftharpoons 2\text{t}$. It then follows that

$$\delta_{\text{obsd}} = \frac{\delta_b + \delta_f K^c/[t]}{1 + \{K^c/[t]\}} \quad \text{and} \quad \frac{K^c}{[t]} = \frac{\delta_b - \delta_{\text{obsd}}}{\delta_{\text{obsd}} - \delta_f} \quad (1)$$

where δ_b and δ_f are the $^1\text{H}_\text{O}$ chemical shifts for hydrogen bonded in the ring and the solvated monomers, respectively. Let a represent the molar concentration of the solute if it were all present as the dimer, and α is its degree of dissociation. Then

$$[t] = 2a\alpha; \quad K^c/[t] = \frac{2\alpha}{1-\alpha}, \quad \text{while} \quad K^c = \frac{4a\alpha^2}{1-\alpha} \quad (2)$$

(ii) Extrapolation of the chemical shifts observed for CDCl_3 solutions indicates that $\delta_b = 12.30$ ppm and $\delta_f = 8.50$ ppm. For a 2% solution, $a = 2.65 \times 10^{-4}$ mol cm⁻³. Then straightforward calculations of α and K^c for the five temperatures listed in Table I gave values for a plot of $\ln K^c$ vs. $1/T$, from which we deduced $\Delta H^\circ = 10.2 \pm 0.6$ kcal/mol and $\Delta S^\circ = 18.1 \pm 2$ eu at 276 K. These values are within the range reported for the dissociation of aliphatic acids in polar solvents.¹⁸ Assumption (i) is not unreasonable. To estimate the concentration of the [D] isomer, assume that for $\text{R} \rightleftharpoons \text{D}$ the enthalpy and entropy increments are midway between [R] and [2t]. Then $\Delta H^\circ_{\text{R/D}} \approx 5$ kcal mol⁻¹ and

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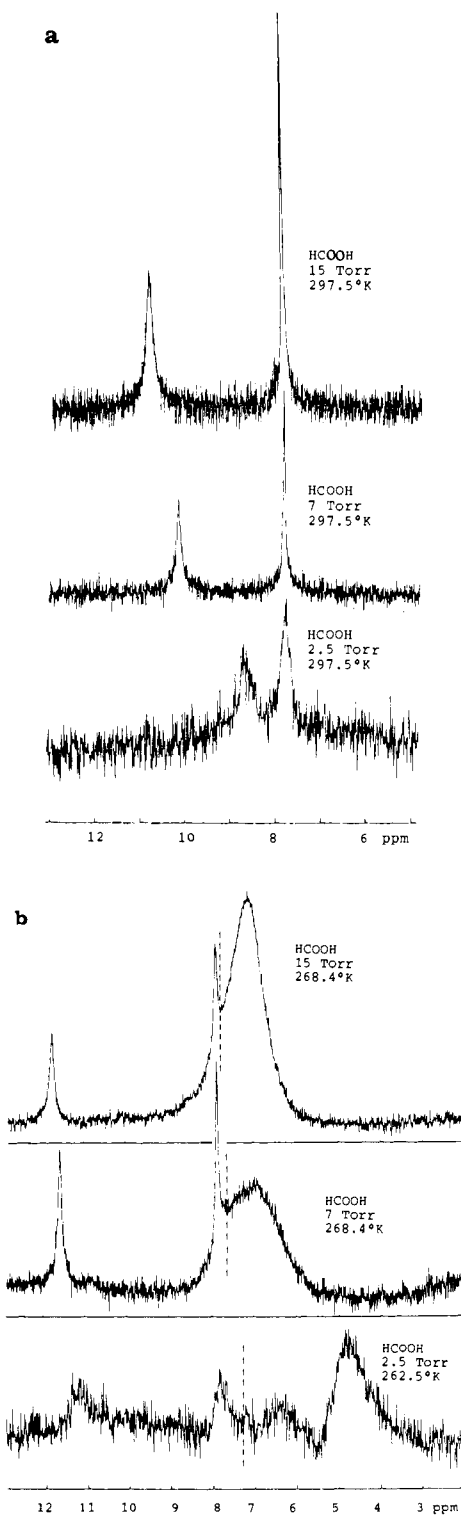


Figure 2. NMR spectra of gaseous formic acid. (a) Pressure dependence at 297.5 K; (b) Pressure dependence at 268–262 K.

$\Delta S^\circ_{R/D} \approx 9$ eu at 296 K. Hence $K^c_{296}(R/D) = 1.9 \times 10^{-2}$.

Gas-Phase Studies

NMR spectra of the gas were recorded at 15 ± 0.5 , 7 ± 0.5 , and 2.5 ± 0.3 torr (measured at room temperature). The $^1\text{H}_C$ line appeared at ≈ 7.8 ppm (compared to ≈ 8.1 ppm in solutions). Its position remained independent of sample pressure or temperature. However, the $^1\text{H}_O$ resonances were strongly dependent on both. When the temperature was lowered they shifted to lower fields and when the pressure was lowered they shifted toward higher fields, as expected for changing ratios of monomer/dimer. These data are summarized in Table II; the spectra are shown in Figure 2, a and b. Assuming that the chemical shifts for the

Table II. $^1\text{H}_O$ Resonances in HCOOH (Gas Phase)

pressure (torr) at 296 K	temp (K)	δ_{obsd} (ppm)	\approx fwhm (Hz)	δ_{calcd}
15	297.5	10.7	44	11.0
15	268.4	11.7	36	11.9
7	297.5	10.1	31	10.6
7	268.4	11.5	31	11.7
2.5	297.5	(≈ 8.7)	91	9.9
2.5	262.5	11.2	186	11.5

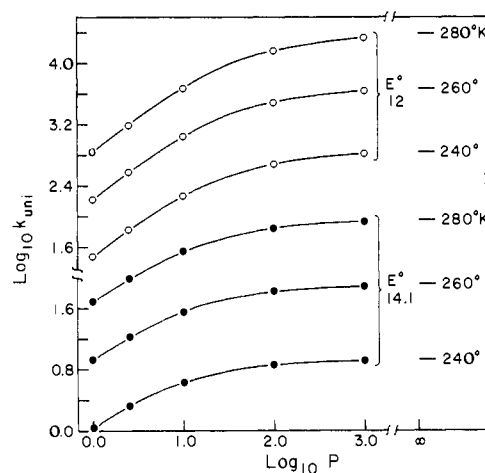


Figure 3. RRKM curves for the dissociation of $(\text{HCOOH})_2 \rightarrow 2\text{HCOOH}$ for three temperatures (280, 260, 240 K) and for $E^\circ = 14.1$ (lower set); 12.0 kcal mol $^{-1}$ (upper set).

$^1\text{H}_O$ resonance are determined by the rapid exchange of the hydroxyl protons between the t-monomer and R-dimer and the accepted values⁹ for ΔH° and ΔS° (298 K), one may readily calculate the expected chemical shifts, with $\delta_{\text{free}} = 8.4$ ppm and $\delta_{\text{bound}} = 12.3$ ppm, for comparison with δ_{obsd} . These are also listed in Table II; the agreement is acceptable.

Inspection of the 297.5 K spectra (Figure 2a) shows that when the pressure was lowered to 2.5 torr both the $^1\text{H}_C$ and $^1\text{H}_O$ resonances broadened, consistent with the general trend for line broadening with pressure reduction; some loss by diffusion also may have contributed to this effect. Spectra taken at 268.4 and 262.5 K showed broad "condensation" peaks on the high-field side (below ≈ 7.5 ppm) of the $^1\text{H}_C$ resonances. This general phenomena was previously observed with other compounds at temperatures just below their condensation points. Even after more than 50 000 scans the S/N ratio for the spectrum of 2.5 torr at 262.5 K did not improve significantly. Were there no condensation at this temperature and pressure only 11% of the gas would be present as monomer. Again it appears that the relaxation time for dissociation/association is somewhat shorter than the NMR relaxation time so that only an upper limit for τ_{chem} can be established at present. For

$$[\text{R}] \frac{k_r}{k_f} 2[t]$$

$$\tau_{\text{chem}}^{-1} = k_f^{-1} [1 + 2[t]/K^c] \quad [3]$$

The possibility that trimers or higher polymers are present at these low pressures can be discounted;¹⁹ also, an argument analogous to that presented above for the 2% solutions eliminated consideration of the [D] structures; indeed, we estimated that for the gas phase $[\text{D}]/[\text{R}] < 4 \times 10^{-3}$.

Since the structures and vibrational frequencies of both the [t] and [R] structures are well established,^{8,20} one may calculate τ_{chem} for specified E° 's via RRKM. In the transition structure, the

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O··H··O distance was increased to 3.50 Å, from 2.70 Å in (R), and $\nu(\text{O}\cdots\text{O}$ stretch, at 248 cm^{-1}) was taken as the reaction coordinate. The other interatomic distances and vibrational frequencies were assumed to be mean values between those of [t] and [R], with $E^\circ = 14.1 \text{ kcal mol}^{-1}$; a collision cross-section of 6.86 Å was estimated; $\lambda = 1$, and the Whitten-Rabinovitch state count was used. The results for $\log k_{\text{uni}}$ vs. $\log P$ (torr) are plotted in Figure 3. Below 10 torr the system follows second-order kinetics. At $T = 260 \text{ K}$ and $P = 2.5 \text{ torr}$, $k_{\text{uni}} = 17 \text{ s}^{-1}$. Another set of curves calculated with $E^\circ = 12 \text{ kcal mol}^{-1}$ gave $k_{\text{uni}} [T = 260; P = 2.5 \text{ torr}] = 380 \text{ s}^{-1}$. At 260 K, $K^{(p)} = 1.036 \times 10^{-4} \text{ atm}$ and $K^{(c)} = 4.856 \times 10^{-9} \text{ mol cm}^{-3,9}$ and for a room temperature fill of 2.5 torr, $[t]_{\text{eq}}^{260} = 2.44 \times 10^{-8} \text{ mol cm}^{-3}$. Hence $\tau_{\text{chem}}^{\text{calcd}}(E^\circ = 12) = 2.38 \times 10^{-4} \text{ s}$ and $\tau_{\text{chem}}^{\text{calcd}}(E^\circ = 14.1) = 5.32 \times 10^{-3} \text{ s}$.

The absence of a characteristic coalescence feature in the many numerous scans we recorded indicates that for the $^1\text{H}_\text{O}$ exchange $\tau_{\text{NMR}} \leq 2 \times 10^{-4} \text{ s}$, since $\Delta\nu = 1170 \text{ Hz}$ at 300 MHz for the monomer vs. dimer chemical shifts. This is not consistent with $E^\circ = 14.1 \text{ kcal mol}^{-1}$; rather it indicates that E° is somewhat less than 12 kcal mol^{-1} . However, one can argue that no serious discrepancy with the thermochemical value exists. Note that $E^\circ = \Delta H^\circ_0 = \Delta H^\circ_{300} - \int_0^{300} \Delta C_p dT$. The heat capacity correction

term is about 1.5 kcal, which may be added to the negative extreme of the quoted error limit (-1.5 kcal).

Our conclusions are the following: (a) There is no detectable barrier to dissociation of the dimer. In that respect the present data are more definitive than the conclusion reached for the $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$ dissociation.²¹ (b) It is likely that a factor of 5-10 increase in NMR sensitivity would permit determination of the dimer/monomer dissociation relaxation time. (c) At pressures below 10 torr, RRKM calculations indicate that the dissociation follows second-order kinetics; i.e., upon association of two [t] monomers the dimer must get de-excited by collision with the third body within less than a nanosecond.

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Resonance Raman Studies of the Excited Electronic States of $(\text{CN})_5\text{Fe}^{\text{III}}(\text{imidazole})^{2-}$ and $(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{imidazole})^{3+}$

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Abstract: UV and visible wavelength resonance Raman spectra and Raman excitation profiles were used to assign the electronic transitions of the imidazole (imH) complexes of $(\text{CN})_5\text{Fe}^{2+}$ and $(\text{NH}_3)_5\text{Ru}^{3+}$. This study demonstrates, for the first time, the ability of resonance Raman excitation profiles to distinguish between the π orbitals involved in imidazole-metal charge-transfer transitions (LMCT). LMCT transitions observed in the absorption spectrum at 475 (Fe) and 425 nm (Ru) involve the imidazole π_1 orbital which has major electron density associated with the carbon atoms of the ring. The 403 (Fe) and 297 nm (Ru) LMCT transitions involve transitions from the π_2 imidazole orbital which has high electron density associated with the nitrogen atoms. The imidazole ring modes of the $(\text{CN})_5\text{Fe}(\text{imH})^{2-}$ and $(\text{NH}_3)_5\text{Ru}(\text{imH})^{3+}$ complexes are selectively enhanced by these LMCT transitions. The Fe complex has an additional absorption band at 356 nm that is not present in the Ru complex. Excitation within this band results in the exclusive enhancement of the $\text{C}\equiv\text{N}$ stretch and a broad low-frequency $\text{Fe}-(\text{C}\equiv\text{N})$ vibration; thus, the 356-nm absorption band is assigned to a $d\pi(\text{Fe}) \leftarrow \text{CN}$ LMCT. The $\text{C}\equiv\text{N}$ stretch is also enhanced within the 403 and 475 nm absorption bands which indicate a strong mixing of the iron and cyanide π orbitals. From the frequency sensitivity to imH deuteration and methyl substitution we tentatively assign the 265- cm^{-1} vibration of $(\text{CN})_5\text{Fe}(\text{imH})^{2-}$ to a $\text{Fe}-\text{N}(\text{imH})$ stretching vibration. It is unlikely that excitation into similar LMCT transitions in heme proteins such as hemoglobin will result in sufficient Raman intensity to permit studies of proximal histidine-heme interactions.

The unique ability of resonance Raman spectroscopy to study the coordination environment of transition metals in proteins derives from its high selectivity and sensitivity.¹ Raman excitation within charge-transfer transitions gives a selective enhancement of internal ligand and metal-ligand stretching vibrations. These data provide important information concerning protein active sites. In addition to its utility as a structural probe of metal sites in proteins, resonance Raman spectroscopy, particularly resonance Raman excitation profiles, provides a powerful technique to aid in the assignment of electronic transitions. Resonant excitation

within an absorption band results in the enhancement of only those modes which are coupled to the electronic transition.²

Imidazole complexes of transition metals are of particular biological interest because the imidazole side chain of the amino acid histidine often binds to metal centers in proteins. The interest in iron-imidazole bonding and interactions derives in part from the ubiquitous presence of imidazole-iron porphyrin complexes in heme proteins and the possible involvement of this linkage in the cooperativity mechanism of hemoglobin.³

This work characterizes the resonance Raman excitation profile of the LMCT transitions⁴ of $(\text{CN})_5\text{Fe}^{\text{III}}\text{imH}^{2-}$ and $(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{imH}^{3+}$ and provides a basis for similar studies on heme

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