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Surface Intervalence Enhanced Raman Scattering from Fe(CN)$_6^{4-}$ on Colloidal Titanium Dioxide. A Mode-by-Mode Description of the Franck-Condon Barrier to Interfacial Charge Transfer.

by

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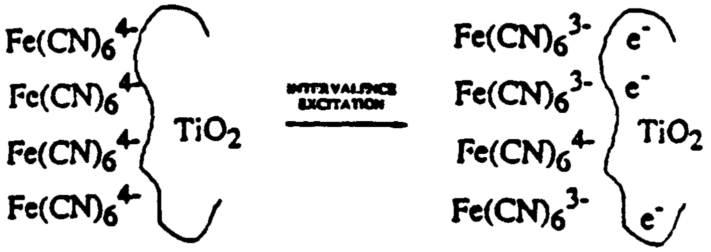
Abstract: The first experimental observation of "surface intervalence enhanced" Raman scattering (*not* SERS) is reported. The transition giving rise to the enhancement is a heterogeneous charge transfer between $Fe(CN)_6^{4-}$ and colloidal titanium dioxide (Vrachnou, et al. J. Electroanal. Chem., 1989, 258, 193). Enhancement effects in the scattering spectrum are interpreted with the aid of recently developed time-dependent analyses. From the analyses a complete, quantitative description of charge-transfer induced vibrational reorganization is obtained (i.e. all force constants, all normal coordinate displacements, and all single-mode components of the vibrational Franck-Condon barrier to charge-transfer are obtained). For the $Fe(CN)_6^{4-}$/colloidal-TiO_2 system, the most significant findings are: a) that a total of ten modes are displaced during interfacial electron transfer, b) that the largest single displacement occurs in a mode associated with a bridging cyanide ligand, and c) that three *surface* modes (Ti-O vibrations) are activated during optical electron transfer.

One of the key requirements in any quantitative description of electron transfer kinetics, in any environment, is an accurate estimate of internal or vibrational reorganization energetics.[1] We have recently shown that complete mode-by-mode descriptions of vibrational reorganization for selected metal-to-ligand[2] and metal-to-metal (or intervalence)[3] charge-transfer events in solution can be obtained by applying time-dependent scattering theory[4,5] to pre- or post-resonance Raman spectra.[6] The quantities obtained are redox-induced normal coordinate displacements (Δ), force constants (f) and individual components (χ_i') of the total vibrational reorganization energy (χ_i). We now wish to report an extension of this methodology to an *interfacial* charge transfer reaction.

The reaction chosen was optical electron transfer from $Fe(CN)_6^{4-}$ to colloidal titanium dioxide:[7,8]



(1)

Following Vrachnou and co-workers,[7] we find that an intense optical absorption exists ($\lambda_{max} \approx 410$ nm, $\varepsilon \approx 5{,}000$ M^{-1} cm^{-1}) for the "surface intervalence" charge transfer reaction in eq. 1. We further find (fig. 1) that Raman scattering spectra can be readily obtained based on near-resonant excitation (488 nm).[9] Control experiments at 514.5 nm (nominally preresonant), at 647.1 nm (off resonance), with ferrocyanide alone, or with colloidal TiO_2 alone, all show the scattering in fig. 1 to be resonantly enhanced (e.g. enhancement factors of at least 20 for the highest energy modes).[10]

The observation of enhancement is of central importance: within the context of the time-dependent theory,[4,5] resonance enhancement (Albrecht A-term scattering) indicates the displacement of normal coordinates in direct response to the pertinent electronic transition (in our case, eq. 1). In the simplest case, the quantitative relationships between scattering intensity (I) and molecular structural changes are:[4]

$$I_1/I_2 = \omega_1^2\,\Delta_1^2/\omega_2^2\,\Delta_2^2 \qquad (2)$$

and

$$\chi_i = 0.5\sum_k \Delta_k^2(\omega_k/2\pi) \qquad (3)$$

where ω is 2π times the vibrational frequency and the summation is over all modes which are significantly resonantly enhanced. If a local mode approximation is appropriate, absolute bond length changes ($|\Delta a|$) can also be obtained:[2,4]

$$(|\Delta a|) = \left(\Delta^2\hbar/\mu\omega b\right)^{1/2} \qquad (4)$$

In eq. 4, μ is the reduced mass and b is the bond degeneracy.

Table 1 lists the relative intensities, unitless normal coordinate displacements and bond-length changes obtained for resonance enhanced modes. Absolute Δ and Δa values were derived by assuming that the changes in length for nonbridging Fe-C bonds equalled those determined crystallographically for free $Fe(CN)_6^{3-/4-}$.[12] Mode assignments were made by analogy to $Fe(CN)_6^{4-}$,[13] $(H_3N)_5Ru\text{-}NC\text{-}Fe(CN)_5^{1-}$, $(H_3N)_5Os$-

$NC\text{-}Fe(CN)_5^{1-}$ and related systems,[3] and will be described in greater detail elsewhere. From the table, a number of points are worth noting: 1) The total number of modes (or types of bonds) displaced is surprisingly large (ten) indicating that even the simplest of interfacial redox reactions may entail substantial complexity in vibrational activation. 2) As seen for related binuclear metal systems (in solution),[3] bridging modes suffer the greatest displacement, with the $C\equiv N$ bridging mode providing the largest single contribution to the vibrational barrier. 3) Remarkably, three *surface* modes are enhanced and therefore displaced during optical electron transfer. This last observation is unprecedented experimentally and is at odds with most, if not all, existing theoretical views of interfacial electron transfer.

While the mode assignments in Table 1 are reasonably well established, questions do arise regarding the possibility of more than one type of binding geometry (e.g. doubly-bridged) and the degree of protonation of the bound ferrocyanide. We performed a number of control experiments where: (1) $Fe(CN)_6^{4-}$ and colloidal TiO_2 concentrations were substantially varied. (2) The pH was varied between 1 and 3. (3) Multiple excitation wavelengths were used in resonance. (4) An isotope study using a 7:1 dilution in D_2SO_4/D_2O was completed.[14] Interestingly, all of these experiments led to no change in relative Raman intensities or frequency shifts. These results, therefore, tend to support the notion that only one type of complexed ferrocyanide species exists, which apparently is unprotonated, and is bound to titanium via a single-cyanide ligand.[14]

Finally, the possibility of unwanted scattering from either a Prussian blue or titanate/$Fe(CN)_6^{4-}$ species was considered. We eliminated the Prussian blue problem by: (a) using $Os(CN)_6^{4-}$ in place of $Fe(CN)_6^{4-}$ with similar results, (b) purposely making the Prussian blue complex which absorbs in the red and showing that it is not present in our absorption spectrum, and (c) proving that no enhancement occurs in the $Fe(CN)_6^{4-}$/colloidal-TiO_2 solution at 647.1 nm (where Prussian blue would absorb). The second problem, titanate formation during preparative $TiCl_4$ hydrolysis, can be effectively eliminated by dialysis.[7] This was confirmed by an electrochemical experiment (supplementary material) in which redox-active $Fe(CN)_6^{4-}$ (i.e. free or titanate bound) was shown to be absent from $Fe(CN)_6^{4-}$/dialyzed-colloid solutions, but present in intentionally prepared $Fe(CN)_6^{4-}$/titanate solutions.[15]

Supplementary Material Available: One figure showing differential pulse voltammograms for $Fe(CN)_6^{4-}$/colloidal-TiO_2 and $Fe(CN)_6^{4-}$/titanate solutions. Ordering information is given on any current masthead page.

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References

1. For general reviews see: (a) Sutin, N. Prog. Inorg. Chem., 1983, 30, 441. (b) Marcus, R. A.; Sutin, N. Biochim. Biophys. Acta 1985, 811, 265. (c) Newton, M. D.; Sutin, N. Ann. Rev. Phys. Chem., 1984, 35, 437.
2. Doorn, S. K.; Hupp, J. T. J. Am. Chem. Soc., 1989, 111, 4704.
3. (a) Doorn, S. K.; Hupp, J. T. J. Am. Chem. Soc., 1989, 111, 1142. (b) Doorn, S. K. Ph.D. Dissertation, Northwestern University, 1990.
4. (a) Heller, E. J.; Sundberg, R. L.; Tannor, D. J. Phys. Chem. 1982, 86, 1822, (b) Tannor, D. J.; Heller, E. J. J. Chem. Phys. 1982, 77, 202. (c) Lee, S. Y.; Heller, E. J. J. Chem. Phys. 1977, 71, 4777. (d) Heller, E. J. Acc. Chem. Res. 1981, 14, 368. (e) Morris, D. E.; Woodruff, W. H. J. Phys. Chem., 1985, 89, 5795.
5. See also: (a) Warshel, A.; Dauber, P. J. Chem. Phys. 1977, 66, 5477. (b) Myers, A. B.; Mathies, R. A. in "Biological Applications of Raman Spectroscopy", T. G. Spiro, Ed.; John Wiley and Sons: New York, 1987; Vol. 2. (c) Schomacher, K. T.; Bangcharoenpaurpong, O.; Champion, P. M. J. Chem. Phys., 1984, 80, 4701. (d) Hizhnyakov, V.; Tehver, I. J. Raman Spectrosc. 1988, 19, 383.
6. Related experimental applications of time-dependent Raman scattering theory: (a) Tutt, L.; Zink, J. I. J. Am. Chem. Soc., 1986, 108, 5830. (b) Zink, J. I.; Tutt, L.; Yang, Y. Y. ACS Symp. Ser. 1986, 307, 39. (c) Yang, Y. Y.; Zink, J. I. J. Am. Chem. Soc. 1985, 107, 4799. (d) Tutt, L.; Tannor D.; Heller, E. J.; Zink, J. I. Inorg. Chem. 1982, 21, 3858. (e) Zink, J. I. Coord. Chem. Rev. 1985, 64, 93. (f)

Truhlson, M. O.; Dollinger, G. D.; Mathies, R. A. J. Am. Chem. Soc. 1987, 109, 586.

7. Vrachnou, E.; Grätzel, M.; McEvoy, A. J. J. Electroanal. Chem. 1989, 258, 193.

8. Colloidal TiO_2 sols were prepared following the method used in ref. 7. We found that agitation and slow addition of potassium ferrocyanide solutions to the dialyzed and diluted colloid produced stable charge transfer assemblies. For Raman studies (excitation at 457.9, 488.0, 514.5 and 647.1 nm) the colloidal sols contained approximately 10^{-4} moles of $Fe(CN)_6^{4-}$ per gram of TiO_2; higher loadings led to sol aggregation then precipitation. Ferrocyanide concentrations ranged from 0.1 to 1.0 mM. In a few experiments NO_3^- or methanol was added as an internal intensity standard. The sol pH was varied between 1 and 3 (chiefly by varying dialysis times and the number of dialysis steps) with no variations found in the enhanced scattering spectra. It should be noted that at the low pH's used in this study, polyvinyl alcohol (a common colloid stabilizer) was not needed.

9. Raman spectra were obtained with a windowless flow cell under an argon blanket. Chromophore concentrations were chosen so as to minimize complications from self absorption. Typically, a bandpass of 9 cm^{-1} was employed with 40 to 60 mW of incident excitation power. For weak portions of the spectrum, signals were sometimes averaged (with appropriate checks for system drift) for as long as twenty hours. We note further that background counts in the low energy end of the spectrum (ca. 750 to 300 cm^{-1}; see fig. 1)

were often as high as 5,000 per second, rendering signal extraction somewhat difficult.

Our results stand in marked contrast to those of Umapathy, McQuillan and Hester (Chem. Phys. Lett., 1990, 170, 128) who very recently reported observing only the two highest frequency modes seen in our spectrum. The precautions described above no doubt account for the exceptional differences between our findings and those reported elsewhere.

10. In addition, very weak, unenhanced modes at 656 and 920 cm^{-1} were occasionally found, as was a stronger mode (also unenhanced) at 1641 cm^{-1}. Lack of enhancement indicates lack of participation of these modes in vibrational reorganization.

11. Intensities have been corrected for residual self absorption (Shriver, D. F.; Dunn, J. B. R. Appl. Spectrosc. 1974, 28, 319) and for ν^4 attenuation effects.

12. Swanson, B. I.; Hamburg, S. I.; Ryan, R. R. Inorg. Chem., 1974, 13, 1685.

13. Jones, L. H.; Memering, M. N.; Swanson, B. I. J. Chem. Phys., 1971, 54, 4666.

14. If, in fact, two cyanide ligands serve as bridges, Δa ($\nu_{C\text{-}N}$ bridge) decreases to 0.032 Å; most other Δa values would be diminished by about 10%.

15. The source of titanate was the outer portion of a colloidal-TiO_2 dialysis solution. See ref. 7 for related experiments.

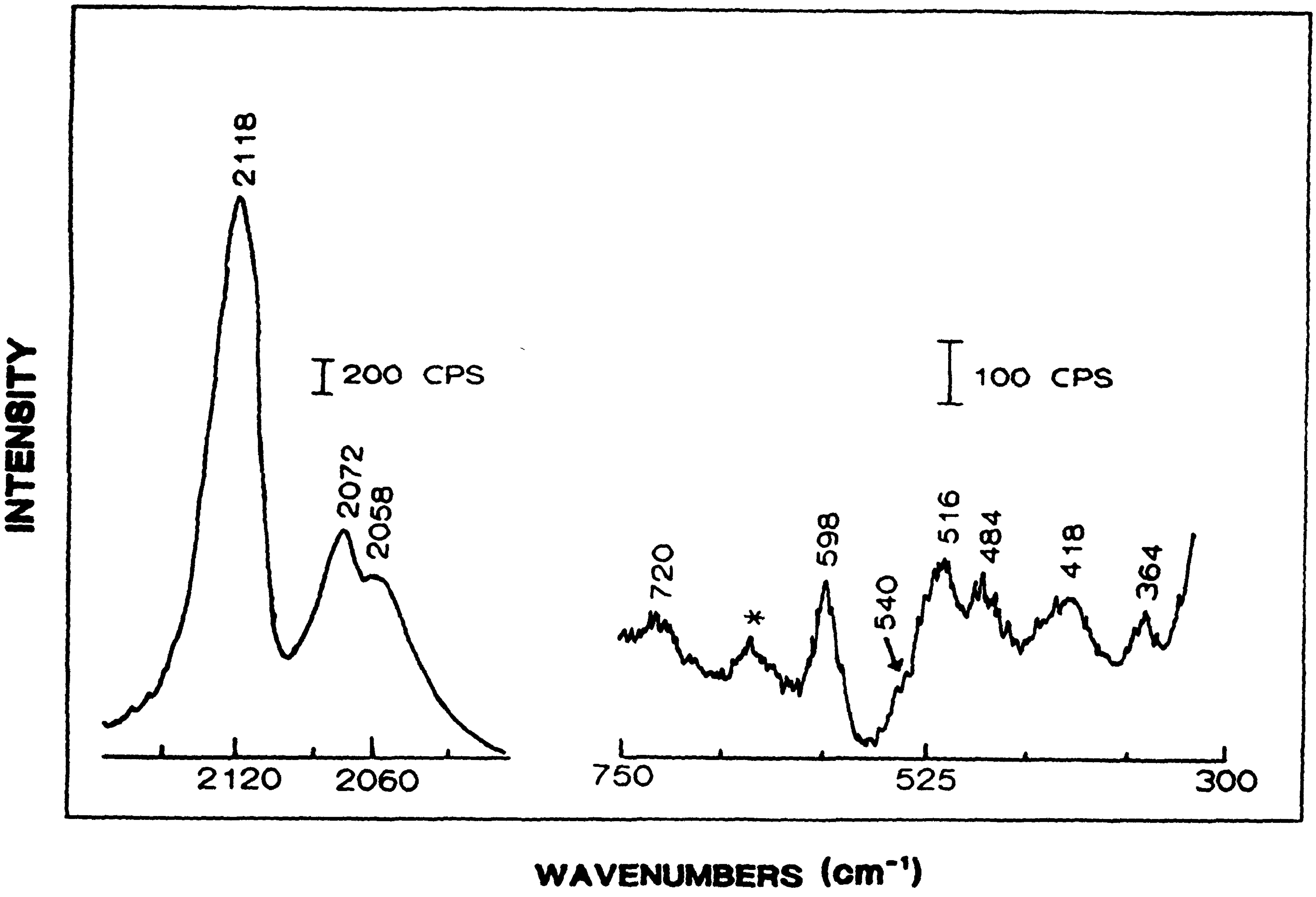
Table 1. Spectroscopic, structural and reorganizational parameters for electron transfer from $Fe(CN)_6^{4-}$ to colloidal TiO_2.

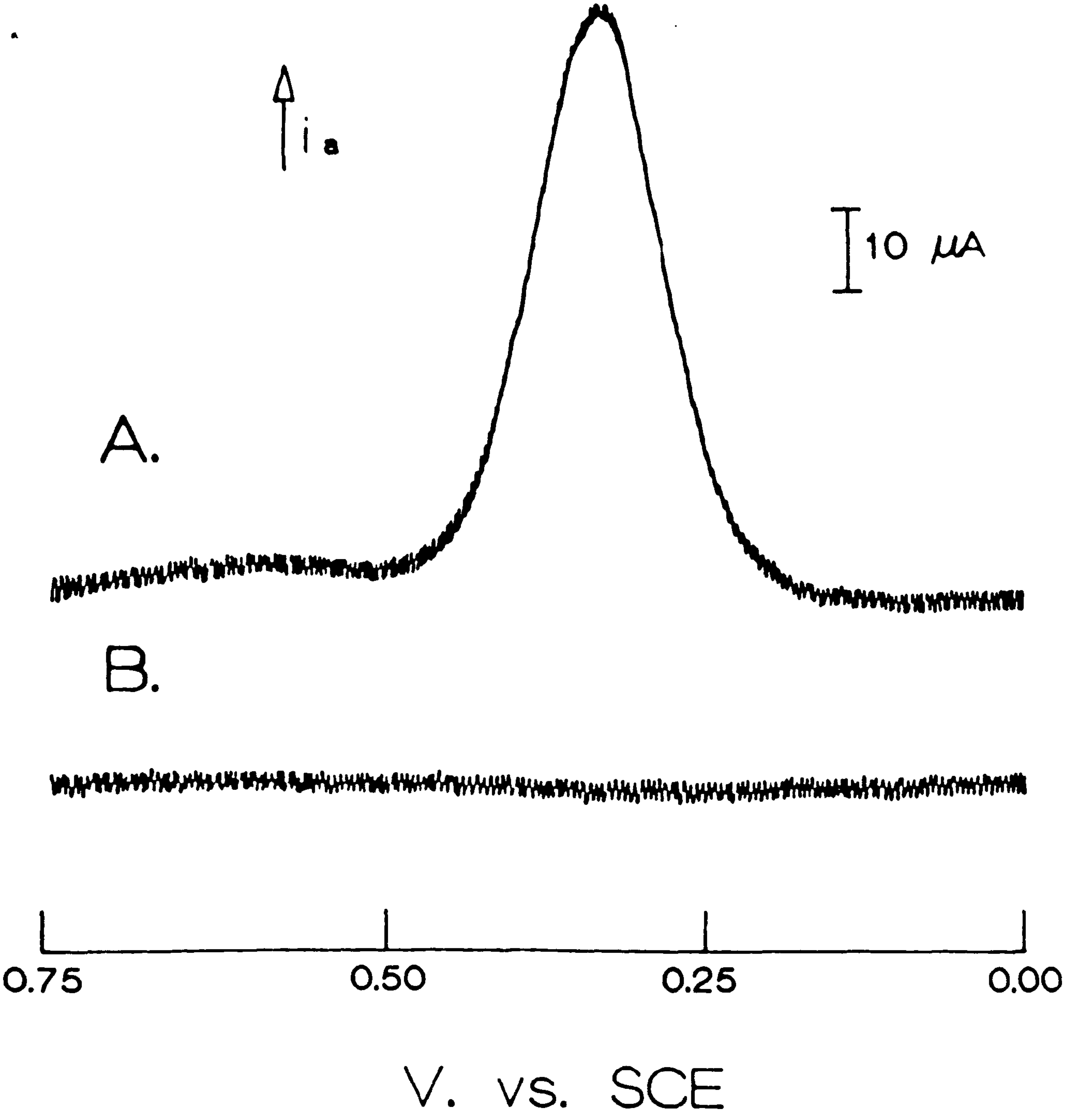
Mode	Relative Intensity[a,b]	Δ^2	$\lvert \Delta a \rvert$	χ_i	Assignment
2118 cm^{-1}	20.0	0.95[c]	0.048 Å	1000 cm^{-1}	$\nu_{C\text{-}N}$ bridge
2072	6.61	0.33	0.014	340	$\nu_{C\text{-}N}$ radial
2058	5.44	0.27	0.026	280	$\nu_{C\text{-}N}$ terminal
720	0.27	0.11	?	40	?
598	1.00	0.59	0.026[d]	180	$\nu_{Fe\text{-}C}$
540	0.33	0.24	0.039	60	$\nu_{Fe\text{-}C}$ bridge
516	1.12	0.89	e	230	$\nu_{Ti\text{-}O}$
484	0.90	0.82	e	200	$\nu_{Ti\text{-}O}$
418	0.56	0.69	e	140	$\nu_{Ti\text{-}O}$
364	0.27	0.43	0.059	80	$\nu_{Ti\text{-}N}$

a. Depolarization studies indicate that all modes, with the possible exception of modes at 540 and 720 cm^{-1} (too weak to determine with certainty), are totally symmetric. b. Within the experimental uncertainty, *relative* intensities are unaffected by changes in excitation wavelength. c. All values scaled to the value for Δ^2 at 598 cm^{-1}. d. Taken from (or taken as) the crystallographically determined value[12] for $Fe(CN)_6^{4-/3-}$. e. Value not determined, since the measured normal coordinate displacement (Δ) may entail more than one type of bond length displacement (i.e., a local-mode approximation may not be appropriate).

Caption for Figure 1

Figure 1. Preresonance Raman spectrum of 0.6 mM $Fe(CN)_6^{4-}$/5.8g/L TiO_2 colloid at pH = 2.0 with 488.0 nm excitation. The asterisk at 656 cm^{-1} denotes an unenhanced E_g mode of TiO_2. The mode at 540 cm^{-1} is real and is more convincingly resolved in experiments performed at 457.9 nm.


2118
200 CPS
2072
2058
2120
2060
720
*
598
540
516
484
418
364
100 CPS
750
525
300
INTENSITY
WAVENUMBERS (cm⁻¹)



Supplemental Figure. Differential pulse voltammograms of (A) $Fe(CN)_6^{4-}$/titanate solution prepared from the outer dialysis water, pH = 2.0, 0.65 mM $Fe(CN)_6^{4-}$, $E_{1/2}^{ox}$ = 0.33 V; (B) $Fe(CN)_6^{4-}$/Colloidal-TiO_2 assembly prepared from the inner dialyzed solution. The experimental conditions are as follows: scan/rate = 5 mV s^{-1}, pulse amplitude = 5 mV, pulse width = 0.5 sec. The electrode material used was glassy carbon.