would then be available for adsorption of guest molecules. In addition, the internal surfaces of the intercalated imogolite tubes represent a second type of surface for guest molecule adsorption.

The presence of regular microporosity for the montmorillonite complex was indicated by Langmuir-type adsorption isotherms for adsorbates with kinetic diameters (<8.6 Å). The pore volume observed for water as an adsorbate (2.65 Å kinetic diameter) was 0.14 cm^3/g. Nitrogen (3.64 Å) and benzene (5.84 Å) both gave a pore volume of 0.094 ± 0.02 cm^3/g. With 1,3,5-triethylbenzene (8.6 Å) and perfluorotributylamine (10.2 Å) as the adsorbates, the pore volume was reduced to <0.014 cm^3/g. Since these latter adsorbates are not expected to access the internal channel of the intercalated imogolite, we conclude that the internal surfaces of the tubular silicate contribute substantially to the zeolitic microporosity observed for adsorbates with a kinetic diameter <8.6 Å.

The BET-N_2 surface area for the montmorillonite TSLS was measured as a function of outgassing temperature. For temperatures in the range 125–435 °C, the surface area was 295 ± 15 m^2/g. Outgassing at 500 °C resulted in a reduction in surface area to a value of 92 m^2/g. The loss in surface area was accompanied by the loss of the −79.3 ppm imogolite resonance in the ^{29}Si MAS NMR spectrum and the appearance of an amorphous silica peak at −108 ppm. Thus, the thermal stability of the TSLS complex appears to be determined by the dissociation of the imogolite tubes.

We anticipate that TSLS complexes will be useful for selective absorption and catalysis. The potential of this new family of pillared clays for acid catalysis is suggested by preliminary studies of alcohol dehydration. Ethanol, isopropyl alcohol, and *tert*-butyl alcohol all undergo dehydration over TSLS complexes at temperatures in the range 200–300 °C to afford corresponding olefins.

Acknowledgment. The support of this research by the National Science Foundation through Grant DMR-8514154 and by the Michigan State University Center for Fundamental Materials Research is gratefully acknowledged.

Assignment of a New Conformation-Sensitive UV Resonance Raman Band in Peptides and Proteins

Sunho Song and Sanford A. Asher*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Samuel Krimm and Jagdeesh Bandekar

Biophysics Research Division, University of
Michigan, Ann Arbor, Michigan 48109

Received July 14, 1988

Preresonance Raman specta of *N*-methylacetamide (NMA)[1,2] and polypeptides[2,3] and UV resonance Raman spectra of NMA[4,5] and proteins[6-8] have shown the presence of a band (or bands), generally near 1400 cm^{-1} but in fact varying from 1496 cm^{-1} in NMA[4] to below 1350 cm^{-1} in α-helical poly(L-lysine) (PLL),[2] whose assignment and significance are unclear. Because this band in ionized PLL (at 1391 cm^{-1}) disappears in D_2O solution,[2] it was "tentatively assigned to a coupled vibration of the —NH—CH—CO— group".[2] Other authors have assigned it to the CH_3 antisymmetric bend[1,4] or to the photoinduced cis peptide group[9] in NMA, to the COO$^-$ symmetric stretch in ionized poly(L-glutamic acid) (PGA)[2] and tropomyosin,[8] and to the CH_2 wag or twist in PLL[3] as well as to the CH_2 bend in cytochrome *c*.[7] Experimental studies on NMA (presented here) and on small peptides as well as PGA and PLL,[10] together with a theoretical analysis of the conformational dependence of this band,[11] indicate that it derives from the overtone of amide V (CN torsion plus NH out-of-plane bend). The amide V band, which is normally strong in the infrared but very weak in the Raman spectrum, is sensitive to the polypeptide chain conformation. Thus, the frequency and intensity of this overtone band can be used as a new sensitive probe of secondary structure in proteins.

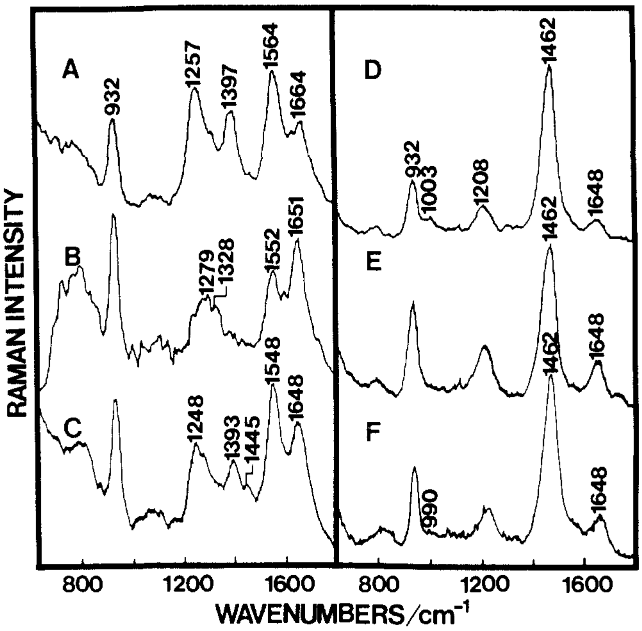

Figure 1. Raman spectra of poly(L-glutamic acid) (0.11 mM) at 218-nm excitation: (A) random coil, (B) α-helix and (C) β-sheet in water, (D) random coil, (E) α-helix and (F) β-sheet in D_2O. A 932-cm^{-1} band is the symmetric stretch of ClO_4^- (0.2 M) used as an internal intensity standard.

The conformation- and deuteration-dependence of this band in PGA[10] are shown in Figure 1 for 218-nm excitation. The amide I, II, and III modes are located near 1650, 1550, and 1250 cm^{-1}, respectively, and shift or disappear as expected[10,12] on N-deuteration. The 932-cm^{-1} band is the symmetric stretch mode of ClO_4^-, used as an internal intensity standard.[13] The putative amide V overtone bands are found at 1397 cm^{-1} in ionized PGA (Figure 1A), near 1330 cm^{-1} in α-PGA (Figure 1B), and at 1445 and 1393 cm^{-1} in β-PGA (Figure 1C). Their disappearance on deuteriation (the 1462-cm^{-1} band is amide II′ and the 1208-cm^{-1} band is due to D_2O) indicates that the mode involved must have an NH component. An assignment to a COO$^-$ mode is excluded by its absence in the deuteriated species, by its Albrecht A-term preresonant state of 194–201 nm,[4,10] corresponding to the amide $\pi \rightarrow \pi^*$ electronic transition, and by its very high cross section compared to that found for COO$^-$ in acetate ion;[11] the fact that strong bands near 1400 cm^{-1} in *normal* Raman spectra of molecules containing COO$^-$ are properly assignable to the COO$^-$

---

(1) Harada, I.; Sugawara, Y.; Matsuura, H.; Shimanouchi, T. *J. Raman Spectrosc.* **1975**, *4*, 91–98.

(2) Sugawara, Y.; Harada, I.; Matsuura, H.; Shimanouchi, T. *Biopolymers* **1978**, *17*, 1405–1421.

(3) Chinsky, L.; Jolles, B.; Laigle, A.; Turpin, P. Y. *J. Raman Spectrosc.* **1985**, *16*, 235–241.

(4) Dudik, J. M.; Johnson, C. R.; Asher, S. A. *J. Phys. Chem.* **1985**, *89*, 3805–3814.

(5) Mayne, L. C.; Ziegler, L. D.; Hudson, B. *J. Phys. Chem.* **1985**, *89*, 3395–3398.

(6) Rava, R. P.; Spiro, T. G. *Biochemistry* **1985**, *24*, 1861–1865.

(7) Copeland, R. A.; Spiro, T. G. *Biochemistry* **1985**, *24*, 4960–4968.

(8) Copeland, R. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1986**, *108*, 1281–1285.

(9) Harada, I.; Takeuchi, H. *Spectroscopy of Biological Systems*; Clark, R. J. H., Hester, R. E., Eds.; Wiley: New York, 1986; pp 113–175.

(10) Song, S.; Asher, S. A. Submitted for publication in *J. Am. Chem. Soc.*, 1988.

(11) Krimm, S.; Song, S.; Asher, S. A. Submitted for publication in *J. Am. Chem. Soc.*, 1988.

(12) Krimm, S.; Bandekar, J. *Adv. Protein Chem.* **1986**, *38*, 181–364.

(13) Dudik, J. M.; Johnson, C. R.; Asher, S. A. *J. Chem. Phys.* **1985**, *82*, 1732–1740.

0002-7863/88/1510-8547$01.50/0

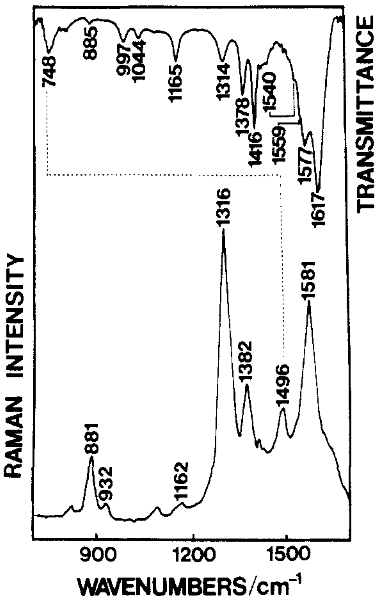

Figure 2. Infrared (upper) and Raman (lower) spectra of aqueous *N*-methylacetamide. Infrared: 1.6 M concentration, run in circle ATR cell (ZnSe rod), 1000 scans on Bomem DA3 at 4-cm^{-1} resolution, water spectrum subtracted. Raman: 0.4 M concentration with 0.2 M perchlorate. The spectral resolution is 7 cm^{-1}.

symmetric stretch does not indicate that an identical assignment is correct for resonance-enhanced bands in this region. As will be discussed in greater detail,[11] the positions of these bands and their shifts with isotopic substitution and conformation are completely consistent with their assignment to the overtone of amide V.[14-16]

This assignment is also consistent with the fact that this band occurs at a much higher frequency (1496 cm^{-1}) in aqueous NMA with 220-nm excitation (ref 4 and Figure 2). The amide V band in the infrared spectrum of neat liquid NMA[17] occurs at 725 cm^{-1}. In aqueous NMA, Figure 2, amide V shifts up to 748 cm^{-1} (an assignment confirmed by its disappearance in D_2O), to exactly half the frequency of the 1496-cm^{-1} Raman band. The 23-cm^{-1} increase in the amide V frequency from neat liquid to aqueous solution indicates that NMA forms a stronger hydrogen bond to the H_2O solvent than to another NMA molecule; this is consistent with the shifts in other amide modes. The assignment to a cis peptide group[9] can be easily excluded because of the expected cis amide frequencies[11] and because our experimental conditions prevent the observation of photochemically generated isomers.[10]

These experiments indicate that the overtone of amide V in the Raman spectra of peptides and polypeptides is selectively resonance-enhanced, even though little or no intensity is observed for the fundamental. Resonance Raman enhancement occurs for normal modes involving atomic displacements that distort the ground electronic state molecular geometry toward that of the resonant excited electronic state.[18,19] This accounts for the enhancement of the amide II and III and particularly the amide II′ modes,[5] which involve C–N bond stretching[12]; the C–N bond length is increased in the π^* excited state. The selective resonance enhancement of the overtone of amide V suggests that, as in ethylene[20] (where the overtone of the torsion is selectively enhanced by the twisted π^* state), the π^* state of the peptide group is twisted. The large CN torsion[12] component of amide V distorts the ground state toward that of the nonplanar excited state. However, as in the case of ethylene,[20] only overtone bands are expected to be enhanced (because of their symmetry). The local symmetry of the CONH fragment of NMA is formally C_s: we expect that this local symmetry will prevent out-of-plane vibrations from coupling efficiently (as fundamentals) to the in-plane $\pi \rightarrow \pi^*$ transition.

We expect that the frequency and intensity of the amide V overtone band will become an important monitor of protein secondary structure. This band is clearly evident in the 200 nm UV Raman spectra of cytochrome *c*,[7] tropomyosin,[8] and myoglobin[21] and shows a strong dependence upon conformation. It will be especially useful since it occurs in a spectral region free from overlap by the strong aromatic amino acid vibrations.

Acknowledgment. This research was supported by NIH Grant 1R01GM30741-07 (S.A.A.) and NSF Grants DMB-8517812 and DMR-8806975 (S.K.). Sanford A. Asher is an Established Investigator of the American Heart Association. This work was done during the tenure of an Established Investigatorship of the American Heart Association, Pennsylvania affiliate.

---

(14) Sengupta, P. K.; Krimm, S.; Hsu, S. L. *Biopolymers* **1984**, *23*, 1565-1594.

(15) Sengupta, P. K.; Krimm, S. *Biopolymers* **1985**, *24*, 1479-1491.

(16) Sengupta, P. K.; Krimm, S. *Biopolymers* **1987**, *26*, S99-S107.

(17) Miyazawa, T.; Shimanouchi, T.; Mizushima, S. *J. Chem. Phys.* **1956**, *24*, 408-418.

(18) Hirakawa, A. Y.; Tsuboi, M. *Science* **1975**, *188*, 359-361.

(19) Tsuboi, M.; Hirakawa, A. Y. *J. Raman Spectrosc.* **1976**, *5*, 75-86.

(20) Ziegler, L. D.; Hudson, B. S. *J. Chem. Phys.* **1983**, *79*, 1197-1202.

(21) Song, S.; Teraoka, J.; Asher, S. A. Manuscript in preparation.

A Reversible Photoredox Reaction: Electron-Transfer Photoreduction of β-Lapachone by Triethylamine

Xiaohong Ci,[1] Rosaly S. da Silva,[2] Joshua L. Goodman,*[,1] David E. Nicodem,[2] and David G. Whitten*[,1]

Department of Chemistry, University of Rochester
Rochester, New York 14627
Instituto de Quimica, Universidade Federal do
Rio de Janeiro, Caixa Postal 1573
Rio de Janeiro 21910, Brasil

Received May 26, 1988

Much attention has been focused on light-induced electron-transfer reactions, interest stimulated at least partially by possibilities that these reactions could be used in energy conversion or storage processes.[3-10] Despite much investigation, examples of recyclable systems based purely on solution photochemical processes and particularly those employing organic reagents are rare.[11-14] Herein, we describe a process based on a simple light-induced electron-transfer reaction and subsequent electron and atom-transfer processes which is at least partially reversible.

---

(1) University of Rochester.

(2) University of Rio de Janeiro.

(3) Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *19*, 1 and references therein.

(4) (a) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215. (b) Ci, X.; Lee, L. Y. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 2536.

(5) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

(6) Schanze, K. S.; Sauer, K. *J. Am. Chem. Soc.* **1988**, *110*, 1180.

(7) McMahon, R. J.; Force, R. K.; Patterson, H. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 2670.

(8) Sinisterra, J. V.; Marinas, J. M. *Tetrahedron* **1988**, *44*, 651.

(9) Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Botton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733.

(10) Gust, D.; Moore, T. A.; Moore, A. L.; Barrett, D.; Harding, L. O.; Makings, L. R.; Liddell, P. A.; De Schryver, F. C.; Van der Auweraer, M.; Bensasson, R. V.; Rougee, M. *J. Am. Chem. Soc.* **1988**, *110*, 321.

(11) Jones, G.; Malba, V.; Bergmark, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 4214.

(12) Delaive, P. J.; Whitten, D. G.; Giannotti, C. *Adv. Chem. Ser.* **1979**, *173*, 236.

(13) Mattay, J.; Gersdorf, J.; Freudenberg, U. *Tetrahedron Lett.* **1984**, *25*, 817.

(14) Krist, K.; Gafney, H. D. *J. Phys. Chem.* **1982**, *86*, 951.