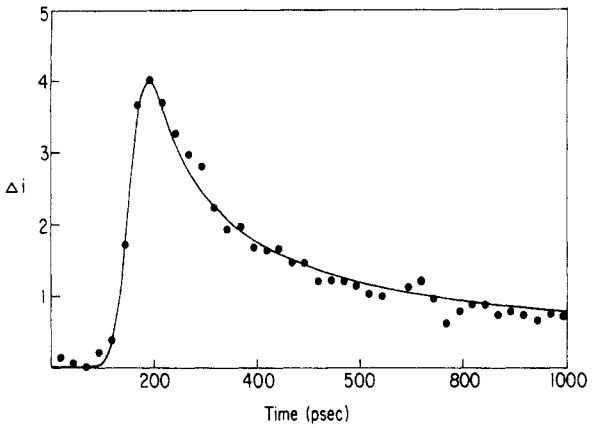

Figure 4. IR-stimulated conductance signal for 0.1 M benzene in hexane excited at 266 nm; T = 225 K. The maximum IR-stimulated signal Δi was approximately twice that of the signal excited by a UV pulse alone. The smooth curve is for an r^2EXP distribution with a mean radius of 57 Å, $D = 2.09 \times 10^{-4}$ cm^2 s^{-1}, r_c = 372.8 Å, and a fwhm for both pulses of 40 ps.

higher efficiency as their radii grow larger. It is surprising that the kinetics of Figure 4 are only marginally slower than those of Figure 3.

The high efficiency of geminate electron scavenging which is seen in Figure 3 is also surprising. While the rate constant for electron scavenging by PFH in hexane does not seem to have been measured, it is expected to be at or near the diffusion-controlled value of other good electron scavengers. Allen, Gangwer, and Holroyd (AGH) have shown[16] that a number of such molecules have rate constants of 1-2 × 10^{12} L mol^{-1} s^{-1} at 295 K. The electron diffusion constant is roughly 10 times smaller at 223 K, and the scavenging rate constant is expected to fall by a factor of 10 as well. Indeed, AGH observed the expected change with temperature for trichloroethylene as scavenger.[16] Using 1 × 10^{11} L mol^{-1} s^{-1} as the rate constant appropriate to 223 K, one estimates a first half-life of 200 ps for electron scavenging by 0.05 M PFH. The scavenging seen in Figure 3 is clearly faster; most of the geminate electrons disappear on a time scale shorter than the pulse-overlap time of about 60 ps. While more work is needed, the result suggests that PFH may act to scavenge nonthermalized electrons. Further work could reveal the time scale on which electrons fall into the low-mobility state characteristic of the liquid at 223 K. We note that Lee and Lipsky have seen evidence of epithermal electron scavenging by perfluorinated hydrocarbons in various hydrocarbon solvents.[17]

The present transient absorption results indicate that, at least for initial pair radii near 50 Å, the IR-stimulated conductivity technique provides a reasonably unbiased view of geminate pair decay kinetics. Further work will be required to assess the detailed shape and possible temperature dependence of the distribution function of initial thermalization lengths.

Acknowledgment. Grant DE-FG02-86ER13592 from the Department of Energy provided partial support for this work; such support does not constitute an endorsement by DOE of the views expressed in the article. We also thank reviewer 2 for making us aware of Hummel's result.[15]

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Selective Enhancement of Proline Raman Signals with Ultraviolet Excitation[1]

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(Received: November 17, 1986; In Final Form: June 24, 1987)

Preresonant Raman spectra of Gly-Pro, Pro-Gly, and *N*-acetylproline methylamide with excitations between 240 and 200 nm are presented. It is shown that, with excitation near 230 nm, vibrations of the X-Pro bond are preferentially enhanced by approximately a factor of 30 relative to vibrations of the normal peptide bond.

The far-UV resonance Raman spectroscopy of protein components has been of considerable recent interest.[2-5] The aromatic amino acids have been studied and analyzed in terms of benzene modes,[5] and *N*-methylacetamide has been studied as a model for the peptide bond, leading to further understanding of the nature of its vibrational modes and the complex excited electronic state manifold of this chromophore.[2] The resonance Raman spectroscopy of the X-proline bond is of particular interest because the structure around the nitrogen in this group distinguishes it from the normal secondary amide peptide bond in terms of its electronic and vibrational spectra. Proline bonds are also of interest because of their implication in studies of protein renaturation kinetics.[6] In particular, the "slow folding" component observed in renaturation is believed to be due to the presence of incorrect X-proline isomers in the unfolded form. There is, however, no direct evidence for this involvement due, in part, to the lack of good spectroscopic techniques that are sensitive to proline isomerization and applicable to proteins. In this study we present preliminary results which may lead to a technique for the detection of cis-trans isomers at X-proline bonds. Specifically, it is demonstrated that the use of radiation near 230 nm results in selective excitation of the resonance Raman spectrum of the peptide linkage to proline relative to that of the normal secondary peptide linkage.

Preliminary studies reported elsewhere[7,8] indicate that there are small but significant differences between the ultraviolet resonance-enhanced Raman spectra of cis and trans X-proline bonds.

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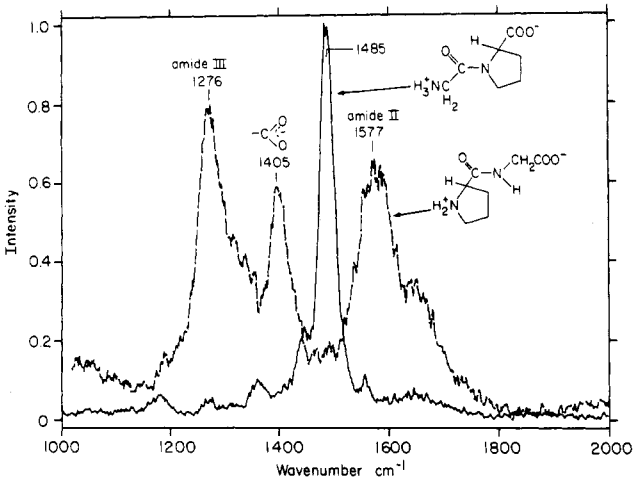

Figure 1. Resonance Raman spectra of prolylglycine (solid line) and glycylproline (dashed line). Both spectra obtained with 218-nm excitation from 10 mM solutions of the dipeptides.

A more significant problem, however, is the detection of one or a few X–proline bonds in the background of other amide vibrations in a similar spectral region. In proteins of current interest such as ribonuclease[6] the bond of interest is only present at a level of 4 per 124. In the present Letter we show that the differences between secondary and tertiary amide electronic properties can be used to selectively enhance the X–proline Raman bands relative to those of other peptide linkages.

Glycylproline and prolylglycine were obtained from the Sigma Chemical Co. and used without further purification. *N*-Acetylproline methylamide was prepared from *N*-acetylproline by reaction with carbonyldiimidazole in $CHCl_3$ followed by reaction with methylamine. The product was purified by ion-exchange chromatography. The sodium sulfate used as an intensity standard[9] was Baker "analyzed" grade. The resonance Raman apparatus was the same as has been described elsewhere.[2,3] The output of a Quanta-Ray DCR 2 Nd:YAG laser, 30 Hz, oscillator only (1064 nm), is passed through nonlinear crystals to generate the second (532 nm), third (355 nm), or fourth (266 nm) harmonics of the laser fundamental. A variety of other wavelengths are then generated by Raman shifting in hydrogen gas at several atmospheres pressure. Power levels range from 220 μJ/pulse at 240 nm to 25 μJ/pulse at 200 nm in an 8–10-ns pulse. A particular shifted line is directed to and loosely focused on a flowing sample stream. The scattered light is collected in a backscattering geometry. Sample solutions were in doubly distilled water with concentrations of peptide of 5–50 mM and of Na_2SO_4 of 0.1–0.5 M. The effects of self-absorption in the relative excitation profile data were found to be negligible.

The resonance Raman spectra of prolylglycine and glycylproline taken with 218-nm excitation are shown in Figure 1. The Pro-Gly spectrum shows predominately the amide II and III modes at 1577 and 1276 cm^{-1}. The $-CO_2^-$ symmetric stretch at 1405 cm^{-1} is also observed. Gly-Pro, on the other hand, shows almost exclusively enhancement of a mode at 1485 cm^{-1}.

Figure 2 shows the resonance Raman spectra of *N*-acetylproline methylamide with various excitation frequencies. With 240-nm excitation we see only the 1485-cm^{-1} mode from the X–Pro amide bond. With higher excitation frequencies we see, in addition, a noticeable amount of the amide II modes from the Pro–X bond.

The spectra of the Pro-Gly and Gly-Pro peptide bonds are quite like those of *N*-methylacetamide and N-deuteriated *N*-methylacetamide.[2] The UV resonance Raman spectrum of *N*-methylacetamide is, like that of Pro-Gly, dominated by the amide II and III modes. These modes are both mixtures of C–N stretch and N–H in-plane bend. Upon deuteriation the frequency of the N–D bend is lowered and so largely decouples these two motions,

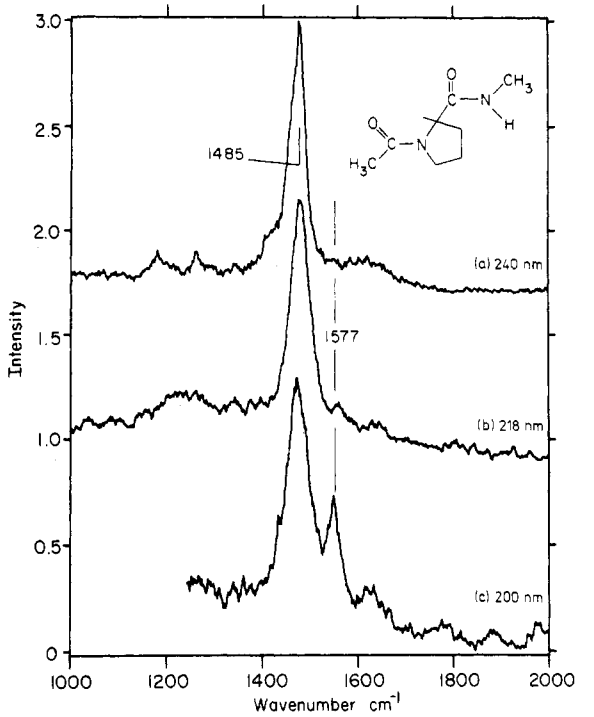

Figure 2. Resonance Raman spectra of *N*-acetylproline methylamide obtained with 240-nm (a), 218-nm (b), and 200-nm (c) excitation. Solutions in water with concentrations of 5–50 mM.

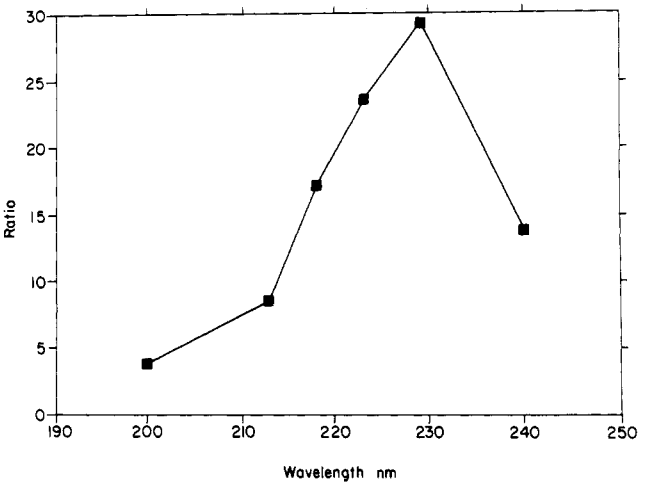

Figure 3. Plot of the intensity of the amide II′ like mode of Gly-Pro relative to the amide II mode of Pro-Gly. Intensities are based on peak height.

yielding the amide II′ and III′ modes.[2,10] The resonance Raman spectrum of *N*-deuterio-*N*-methylacetamide is dominated by the amide II′, C–N stretch, mode. In analogy, we believe that the mode at 1485 cm^{-1} displayed in the Gly-Pro and *N*-acetylproline methylamide is a C–N stretch amide II′ like mode.

A series of spectra of Gly-Pro and Pro-Gly were recorded at various excitation frequencies with sodium sulfate as an internal standard. The intensities of the amide II, III, and II′ modes were then scaled to the intensity of the 981-cm^{-1} band of sulfate, correcting for relative concentrations. The ratio of the amide II′ like intensity to amide II intensity is plotted in Figure 3.[11]

The differential enhancement of this amide II′ like mode in X–Pro linkages relative to the amide II and III vibrations of the normal peptide bond closely follows the difference in the absorption

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spectra of these two chromophores. The $\pi \rightarrow \pi^*$ transition of the X-Pro chromophore is shifted to lower energy relative to that of the normal peptide bond. In addition, there is some apparent enhancement of the amide II' band due to the fact that all of the Raman intensity from the X-Pro chromophore is in this single mode rather than divided between the amide II and III modes.

As a further demonstration of this differential enhancement, the spectra of *N*-acetylproline methylamide obtained with 240- and 218-nm excitation exhibit almost exclusively the amide II' like mode at 1485 cm^{-1}. The spectrum excited with 200-nm radiation has a noticeable amount of the amide II mode. These spectra are almost indistinguishable from synthetic spectra produced by summing those for Gly-Pro and Pro-Gly with appropriate scaling; therefore, this pattern is consistent with the data of Figure 3.

These results show that by tuning the excitation frequency to the 220-240-nm region it is possible to selectively enhance the resonance Raman signal due to X-Pro peptide bonds over the signal due to normal peptide bonds by a factor of about 30. This selectivity may be of use in determining the state of cis-trans isomerism of these bonds.

Acknowledgment. This work was supported by NIH Grant GM 32323 and NSF Grant PCM 8308529.

Apparent Fractional Dimensionality of Uranyl-Exchanged Zeolites and Their Photocatalytic Activity

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The temporal behavior of the intensity of an energy donor in the presence of energy acceptors distributed over a disordered lattice with dilation symmetry is predicted to give information about its fractal dimensionality. Using calculation and simulation, we have recently shown that the same procedure gives an "apparent fractional" dimensionality for lattices with *translational symmetry possessing excluded volumes*. In this Letter, we have experimentally determined the "apparent fractional" dimensionality of four "crystalline" uranyl-exchanged zeolites from the observed decay of the uranyl ion (donor) emission in the presence of europium ions as acceptors. While no correlation is observed between the fractional dimensionality and the fraction of void or the energy-transfer efficiency on these four lattices, it is found that the zeolite with the lowest dimensionality is the most effective in the photocatalytical conversion of isopropyl alcohol to acetone.

Introduction

Recently, studies[1-5] of one-step energy transfer have been discussed both theoretically and experimentally in terms of fractal dimension.[6] Theoretically, Klafter and Blumen[1] (KB) extended the classical results describing the time dependence of a donor emission intensity, $I(t)$, in uniform systems of constant average density of molecules, (i.e., solutions and crystals), to fractal structures with dilation symmetry. In the derivation of their equations, a continuous dilation symmetry (i.e., the open fractal structure containing holes of all sizes) was implied.[3,4] According to the KB equation,[1] a straight line should be obtained for dipolar transfer if log $(-\log I(t))$ is plotted vs. log t, where $I(t)$ is the experimentally observed donor emission intensity at time t. The slope of the straight line gives the fractal dimension of the fractal structure on which the donors and acceptors reside.

In our earlier calculation,[2] we have examined the fit of the simulated time-dependent donor intensity to the KB equation for structures with translational symmetry (i.e., nonfractal), but containing excluded volume which is similar to porous structures. A nearly straight line could be obtained for a finite range of time, which is large compared to the experimentally observed transfer times. From the slope of straight lines, a noninteger, "apparent fractional" dimensionality has been obtained. This has shown that a "fractal-like", but nonfractal type, behavior could be observed for one-step dipolar energy transfer on regular crystalline lattices with excluded volumes. Crystalline zeolites could indeed exemplify a system with porous structure (and thus excluded volumes) with translation symmetry.

In this paper, the results of the decay of the intensity for an energy-transfer donor, uranyl ion (UO_2^{2+}), and an energy acceptor, europium ion (Eu^{3+}), in different zeolite structures (e.g., A, Y, mordenite (Mord), and ZSM-5 zeolites) are analyzed. Because of the differences in the size and the structure of the pores in the different zeolites, the excited donor (uranyl ion) decay shows different temporal behaviors. From the time dependence of the donor intensity plotted according to the KB equation,[1] a noninteger, "apparent fractional" dimensionality has been calculated. In principle, geometric structural information about the distribution of the donor (UO_2^{2+}) and the acceptor (Eu^{3+}) ions can be retrieved from the values of the "apparent fractional" dimension. It is found that at concentrations of 0.005 and 0.095 M for UO_2^{2+} and Eu^{3+}, respectively, the ZSM-5 zeolite has an "apparent fractional" dimensionality near unity, while the others are much larger than unity. The "apparent fractional" dimensionalities are

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