

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 ( $<8.6 \text{ \AA}$ ). The pore volume observed for water as an adsorbate ( $2.65 \text{ \AA}$  kinetic diameter) was  $0.14 \text{ cm}^3/\text{g}$ . Nitrogen ( $3.64 \text{ \AA}$ ) and benzene ( $5.84 \text{ \AA}$ ) both gave a pore volume of  $0.094 \pm 0.02 \text{ cm}^3/\text{g}$ . With 1,3,5-triethylbenzene ( $8.6 \text{ \AA}$ ) and perfluorotriethylamine ( $10.2 \text{ \AA}$ ) as the adsorbates, the pore volume was reduced to  $<0.014 \text{ cm}^3/\text{g}$ . 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  $<8.6 \text{ \AA}$ .

The BET- $\text{N}_2$  surface area for the montmorillonite TSLs was measured as a function of outgassing temperature. For temperatures in the range  $125\text{--}435 \text{ }^\circ\text{C}$ , the surface area was  $295 \pm 15 \text{ m}^2/\text{g}$ . Outgassing at  $500 \text{ }^\circ\text{C}$  resulted in a reduction in surface area to a value of  $92 \text{ m}^2/\text{g}$ . The loss in surface area was accompanied by the loss of the  $-79.3 \text{ ppm}$  imogolite resonance in the  $^{29}\text{Si}$  MAS NMR spectrum and the appearance of an amorphous silica peak at  $-108 \text{ ppm}$ . 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  $200\text{--}300 \text{ }^\circ\text{C}$  to afford corresponding olefins.

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

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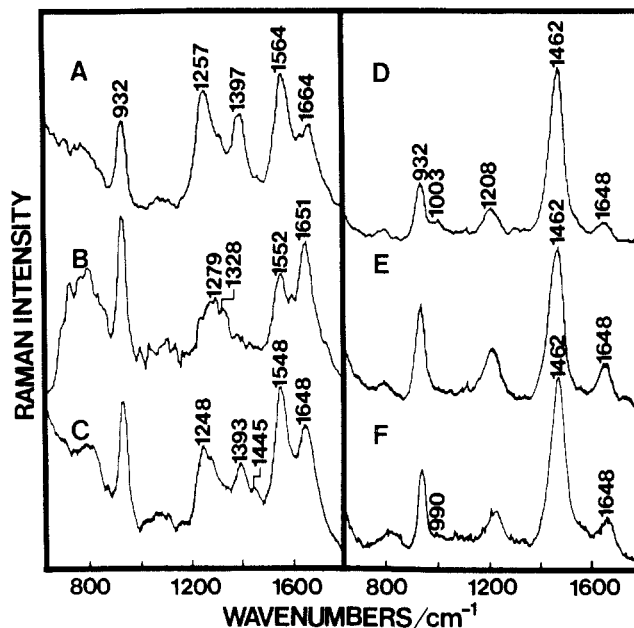
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Preresonance Raman spectra of *N*-methylacetamide (NMA)<sup>1,2</sup> and polypeptides<sup>2,3</sup> and UV resonance Raman spectra of NMA<sup>4,5</sup> and proteins<sup>6-8</sup> have shown the presence of a band (or bands), generally near  $1400 \text{ cm}^{-1}$  but in fact varying from  $1496 \text{ cm}^{-1}$  in NMA<sup>4</sup> to below  $1350 \text{ cm}^{-1}$  in  $\alpha$ -helical poly(L-lysine) (PLL),<sup>2</sup> whose assignment and significance are unclear. Because this band



**Figure 1.** Raman spectra of poly(L-glutamic acid) (0.11 mM) at 218-nm excitation: (A) random coil, (B)  $\alpha$ -helix and (C)  $\beta$ -sheet in water, (D) random coil, (E)  $\alpha$ -helix and (F)  $\beta$ -sheet in  $\text{D}_2\text{O}$ . A  $932\text{-cm}^{-1}$  band is the symmetric stretch of  $\text{ClO}_4^-$  (0.2 M) used as an internal intensity standard.

in ionized PLL (at  $1391 \text{ cm}^{-1}$ ) disappears in  $\text{D}_2\text{O}$  solution,<sup>2</sup> it was "tentatively assigned to a coupled vibration of the  $-\text{NH}-\text{CH}-\text{CO}-$  group".<sup>2</sup> Other authors have assigned it to the  $\text{CH}_2$  antisymmetric bend<sup>1,4</sup> or to the photoinduced cis peptide group<sup>9</sup> in NMA, to the  $\text{COO}^-$  symmetric stretch in ionized poly(L-glutamic acid) (PGA)<sup>2</sup> and tropomyosin,<sup>8</sup> and to the  $\text{CH}_2$  wag or twist in PLL<sup>3</sup> as well as to the  $\text{CH}_2$  bend in cytochrome *c*.<sup>7</sup> Experimental studies on NMA (presented here) and on small peptides as well as PGA and PLL,<sup>10</sup> together with a theoretical analysis of the conformational dependence of this band,<sup>11</sup> 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.

The conformation- and deuteration-dependence of this band in PGA<sup>10</sup> are shown in Figure 1 for 218-nm excitation. The amide I, II, and III modes are located near  $1650$ ,  $1550$ , and  $1250 \text{ cm}^{-1}$ , respectively, and shift or disappear as expected<sup>10,12</sup> on N-deuteration. The  $932\text{-cm}^{-1}$  band is the symmetric stretch mode of  $\text{ClO}_4^-$ , used as an internal intensity standard.<sup>13</sup> The putative amide V overtone bands are found at  $1397 \text{ cm}^{-1}$  in ionized PGA (Figure 1A), near  $1330 \text{ cm}^{-1}$  in  $\alpha$ -PGA (Figure 1B), and at  $1445$  and  $1393 \text{ cm}^{-1}$  in  $\beta$ -PGA (Figure 1C). Their disappearance on deuteration (the  $1462\text{-cm}^{-1}$  band is amide II' and the  $1208\text{-cm}^{-1}$  band is due to  $\text{D}_2\text{O}$ ) indicates that the mode involved must have an NH component. An assignment to a  $\text{COO}^-$  mode is excluded by its absence in the deuterated species, by its Albrecht A-term preresonant state of  $194\text{--}201 \text{ nm}$ ,<sup>4,10</sup> corresponding to the amide  $\pi \rightarrow \pi^*$  electronic transition, and by its very high cross section compared to that found for  $\text{COO}^-$  in acetate ion;<sup>11</sup> the fact that strong bands near  $1400 \text{ cm}^{-1}$  in normal Raman spectra of molecules containing  $\text{COO}^-$  are properly assignable to the  $\text{COO}^-$

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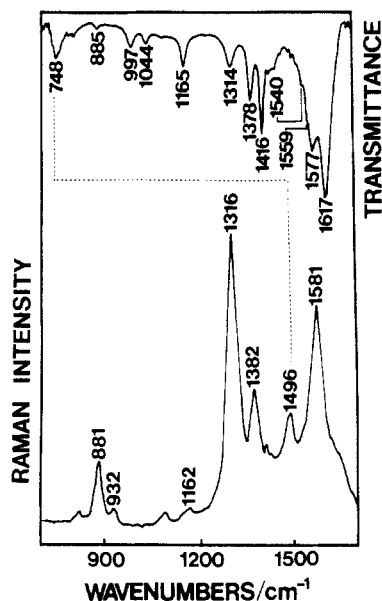
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**Figure 2.** Infrared (upper) and Raman (lower) spectra of aqueous *N*-methylacetamide. Infrared: 1.6 M concentration, run in circle ATR cell (ZnSe rod), 1000 scans on Bomem DA3 at 4-cm<sup>-1</sup> resolution, water spectrum subtracted. Raman: 0.4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

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,<sup>11</sup> 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.<sup>14-16</sup>

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

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.<sup>18,19</sup> This accounts for the enhancement of the amide II and III and particularly the amide II' modes,<sup>5</sup> which involve C-N bond stretching<sup>12</sup>; the C-N bond length is increased in the  $\pi^*$  excited state. The selective resonance enhancement of the overtone of amide V suggests that, as in ethylene<sup>20</sup> (where the overtone of the torsion is selectively enhanced by the twisted  $\pi^*$  state), the  $\pi^*$  state of the peptide group is twisted. The large CN torsion<sup>12</sup> component of amide V distorts the ground state toward that of the nonplanar excited state.

However, as in the case of ethylene,<sup>20</sup> only overtone bands are expected to be enhanced (because of their symmetry). The local symmetry of the CONH fragment of NMA is formally C<sub>s</sub>; 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*,<sup>7</sup> tropomyosin,<sup>8</sup> and myoglobin<sup>21</sup> 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.

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### A Reversible Photoredox Reaction: Electron-Transfer Photoreduction of $\beta$ -Lapachone by Triethylamine

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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.<sup>3-10</sup> Despite much investigation, examples of recyclable systems based purely on solution photochemical processes and particularly those employing organic reagents are rare.<sup>11-14</sup> 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.

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