Observation of an effect of laser light on low-frequency Raman-scattering spectra

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Changes caused in the low-frequency Raman-scattering spectra of amino acids, sugars, and water by the beam from a He–Cd laser, with a wavelength of 4416 Å, have been discovered.

In this letter we report an experimental study of the effect of laser light on the low-frequency region of the Raman scattering spectra of water (doubly distilled), an aqueous solution of glucose and polycrystalline amino acids: valine, leucine, isoleucine, threonine, histidine, and phenylalanine.

In the experiments we use a special illuminator which can excite Raman scattering spectra with either focused or unfocused beams from a He–Cd laser with a wavelength of 4416 Å and a power of 30 mW. The spectra are recorded with DFS-12 double diffraction monochromator. The time required to record spectrograms of the region studied, between 30 and 300 cm^{-1}, is no more than 2 min.

The test material is placed in the illuminator, and its Raman scattering spectra are measured at certain timed intervals. As the spectrograms are recorded, the duration of the laser illumination of the substance thus increases for each successive spectrum.

For all the substances studied we detected changes in the low-frequency part of the spectra as a result of the laser illumination. Figures 1–3 illustrate the results with the Raman spectra of water, glucose, and valine. Curves 1 were obtained by illuminat-

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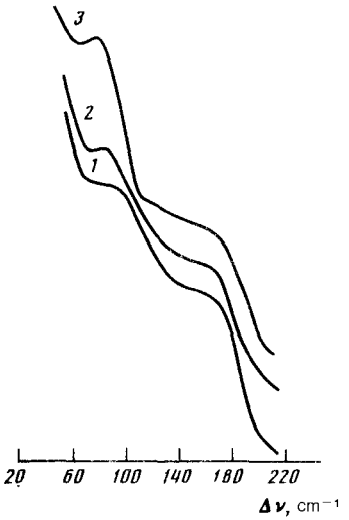

FIG. 1. Raman scattering spectra of doubly distilled water.

ing the samples from the beginning to the end of the recording of the spectra. Curves 2 were taken after a 5-min illumination with the laser light. Curves 3 were recorded after a 20-min illumination; further illumination caused no change in the shapes of these curves. We should point out that the recording of the spectra and the illumination of the substances with the laser light were carried out simultaneously, since the samples were in the field of the laser light at all times. For this reason, the spectra were recorded during a change in the state of the substances; this circumstance complicates the extraction of quantitative information on the time evolution of the processes which are occurring. When the laser beam was blocked, the samples returned to their initial state; the time required for this inverse relaxation was on the order of 20 min. A secondary illumination resulted in the changes in the Raman spectra. When the samples were illuminated with the unfocused laser light, the process was slowed; when the

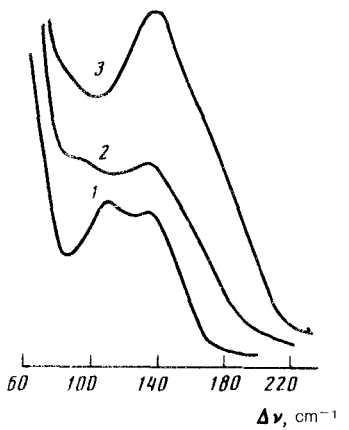

FIG. 2. Raman scattering spectra of an aqueous solution of glucose.

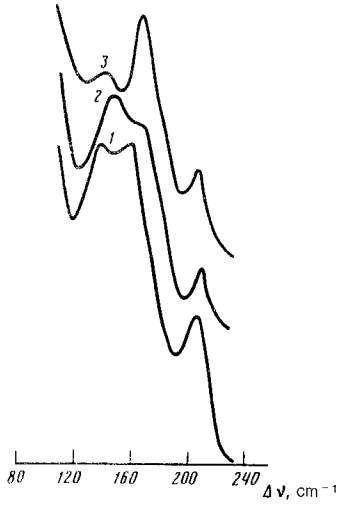

FIG. 3. Raman scattering spectra of polycrystalline valine.

light was additionally attenuated, the process became even slower, without any qualitative changes. Since the energy density of the unfocused laser light was low, the effect of this light cannot be explained in terms of nonlinear effects such as two-photon absorption or the resulting excitation of an electronic state of the molecules. Furthermore, the wavelength of this light is far from resonant electronic absorption of the test substances; that absorption is in the UV part of the spectrum. We can also rule out an explanation of the changes based on heating of the samples, since (first) the laser power was too low and (second) the light was absorbed only weakly by these samples. This conclusion was verified by direct measurements of the temperature of the substances, which did not change at any time in the course of the study. Furthermore, the amino acid samples were heated to 70 °C and held there for 1 h. The Raman spectra did not change when the samples were heated, but we again observed laser-induced changes.

It can be seen from Fig. 1 that the spectra of the water have two weak and broad bands, poorly resolved, with a Rayleigh line, at about 70 cm^{-1} and 150–170 cm^{-1}. These bands correspond to deformation vibrations and valence vibrations of hydrogen bonds.[1] For a supersaturated aqueous solution of glucose, the spectral lines in the interval 100–200 cm^{-1} can also be attributed to vibrations associated with the presence of hydrogen bonds. This comment also applies to the spectra of the amino acids, in which the Raman lines that change lie in the same frequency interval, since their crystal structure is governed by hydrogen bonds.[2–4] It can thus be suggested that prolonged laser illumination changes the structure of hydrogen bonds in the samples. The changes are probably significant, with the result that there is a change in the part of the Raman spectrum which is directly related to the presence of hydrogen bonds. The prolonged occurrence of this process in the forward and backward directions apparently involves a structural relaxation which occurs during a collective change in the structure of hydrogen bonds.

In summary, it has become possible to explain the effect of laser light on systems

with hydrogen bonds and probably systems with other types of intermolecular bonds. Quantitative information of greater accuracy on this effect could be obtained in experiments in which the changes in the vibrational spectra can be observed independently during the laser illumination. This situation could be arranged by studying the IR absorption spectra in the long-wave region.

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