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A scientific session of the Physical Sciences Division of the Russian Academy of Sciences (RAS) was held in the Conference Hall of the Lebedev Physics Institute, Russian Academy of Sciences, on 29 March 2006. The following reports were presented at the session:

(1) **Bunkin A F, Nurmatov A A, Pershin S M** (Wave Research Center at the Prokhorov General Physics Institute, RAS, Moscow) "Coherent four-photon spectroscopy of low-frequency molecular librations in a liquid";

(2) **Simonenko V A** (Russian Federal Nuclear Center — Zababakhin All-Russia Scientific Research Institute of Technical Physics, Snezhinsk, Chelyabinsk region) "Nuclear explosions as a probing tool for high-intensity processes and extreme states of matter: some applications of results";

(3) **Buchelnikov V D, Taskaev S V** (Chelyabinsk State University), **Vasiliev A N** (Lomonosov Moscow State University), **Koledov V V, Khovaylo V V, Shavrov V G** (Institute of Radioengineering and Electronics, RAS, Moscow) "Magnetic shape-memory alloys: phase transitions and functional properties."

A brief presentation of the reports is given below.

PACS numbers: **33.20.–t**, **42.65.–k**, 87.50.Jk
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Coherent four-photon spectroscopy of low-frequency molecular librations in a liquid

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1. Introduction

One of the most urgent problems in the investigation of associated liquids (including liquid water and aqueous solutions of proteins) is the study of the short-range molecular structure of these media, as well as the shape and dimensions of molecular complexes formed by strong intermolecular interactions. This information may be gained from thermal neutron scattering data [1 – 3] and from the optical spectra of low-frequency molecular motion in liquids. The spectra of spontaneous Raman scattering (RS) (in the range $< 100\ \mathrm{cm}^{-1}$) and Rayleigh-wing scattering [4] in the vicinity of zero frequency detuning also contain information about the structure of molecular complexes in liquids, because they depend on intermolecular vibrations and orientational molecular motion. But the use of classical optical spectroscopic techniques [infrared (IR) absorption and RS] in the spectral range from several to $100\ \mathrm{cm}^{-1}$ (0 – 100 THz) runs into several experimental problems.

A separate complicated problem is the spectroscopy of low-frequency vibrational and rotational resonances in the $1-5\ \mathrm{cm}^{-1}$ range. These resonances arise in the media where stable molecular complexes of complex shape may exist with a lifetime far exceeding the hydrogen bond switching time $\sim 10^{-13}$ s. Such resonances may emerge in biological macromolecules consisting, as a rule, of subglobules with a molecular weight of $\sim 10^3$ atomic units connected by peptide or hydrogen bonds [5, 6]. The study of these resonances deepens the understanding of the geometry of linkage between biological molecules and solvent molecules, as well as the mechanics of motion of these complexes.

One of the areas of nonlinear optics spectroscopy that permits an efficient solution to this problem is the four-photon Rayleigh-wing spectroscopy [7, 8]. This approach allows substantially improving the signal-to-noise ratio in low-frequency spectra by phasing the orientational and translational molecular motion in a macroscopic volume with the aid of two laser waves with frequencies ω_1 and ω_2 whose difference $\omega_1 - \omega_2$ is scanned in the range of the Rayleigh wing. The parameter measured in this case is the state of radiation polarization at the frequency $\omega_s = \omega_1 - (\omega_1 - \omega_2)$, whose nonlinear source is of the form [9, 10]

$$\mathbf{P}_i^{(3)} = 6\chi_{ijkl}^{(3)}(\omega_s;\omega_1;\omega_2;-\omega_1)\mathbf{E}_j^{(1)}\mathbf{E}_k^{(2)}\mathbf{E}_l^{(1)*}, \qquad (1)$$

where $\chi^{(3)}$ is the cubic susceptibility of the medium, which is proportional to the correlation function of optical anisotropy fluctuations, and $\mathbf{E}^{(1)}$ and $\mathbf{E}^{(2)}$ are the amplitudes of the interacting fields. The recorded signal intensity is $I_s \propto \left|\chi^{(3)}\right|^2 I_1^2 I_2$. We emphasize that the four-photon interaction between the laser fields and the ensemble of molecules defines the phase of their vibrational and rotational modes in the entire volume of the medium that is simultaneously exposed to radiation with frequencies ω_1 and ω_2.

The spectral resolution in the four-photon spectroscopy is determined by the width of the instrumental function, which is equal, in the first approximation, to the convolution of the spectral linewidths of both lasers with frequencies ω_1 and ω_2. In our measurements (see Sections 2 and 3), these frequencies were in the transparency range of the medium under investigation; the spectral resolution was equal to $\sim 0.1\ \mathrm{cm}^{-1}$.

We emphasize that in the four-photon Rayleigh-wing spectroscopy, with the proper selection of the polarization of the waves $\mathbf{E}^{(1)}$ and $\mathbf{E}^{(2)}$ [6 – 8], measurements are made of the signal proportional to the imaginary part of the cubic susceptibility of the medium: $I_s \sim \left(\mathrm{Im}\,\chi^{(3)}\right)^2$. This circumstance furnishes a significant advantage of four-photon scattering over IR spectroscopy because it opens up the

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possibility of recording, with the use of a single experimental technique, the resonances of electromagnetic radiation absorption for liquid layers up to 30 cm in thickness in a broad (*up to the terahertz range*) spectral range (0 – 30 THz). Without question, this advantage is fundamentally important in the investigation of biomacromolecules, because it permits studying their low-frequency spectra in the natural medium — in aqueous solutions. Interestingly, completely spanning this frequency range (0 – 30 THz) in millimeter and submillimeter spectroscopy requires using several types of radiation sources [1].

Another advantage consists in the possibility of distinguishing between the contributions to the measured signal arising from different mechanisms of orientational relaxation in liquids [12, 13], which are variously manifested in four-photon scattering spectra. In particular, the line broadening centered at the zero frequency, $\omega_1 - \omega_2 = 0$ (the narrow part of the Rayleigh wing), is due to the slow orientational motion of molecular associates, while the contribution of fast rotational molecular motion must show up in the broad part of the Rayleigh wing, $|\omega_1 - \omega_2| > 1$. Several authors [12, 13] have discussed the possibility that there exists orientational relaxation equivalent to the free rotation of molecules in the liquid phase in a time shorter than 1 ps. But to our knowledge, a spectrum consisting of narrow resonances of free molecular rotation in a liquid has not so far been directly recorded.

One of the basic problems arising in liquid-state physics, in particular in the physics of water, consists in providing an explanation of the special features of the hydrogen bond in media whose molecules differ by the value of the nuclear spin of hydrogen atoms. An example of such molecules is the ortho- and paramodifications of water molecules, in which the total spin of hydrogen is either 1 (orthomolecules) or 0 (paraisomers). The ortho- and paraisomers of H_2O molecules in water vapor are in the ratio 3 : 1 in equilibrium conditions. They differ by the rotational spectrum [14] and are readily identified in the gas phase [15]. It was discovered in [15] that water vapor, when passed through a porous material with a developed surface or above the surface of organic (DNA, lysozyme protein) or inorganic compounds [16], is enriched with orthoisomer molecules. The observed selective deviation from the equilibrium ratio was attributed to the fact that the orthoisomer water molecules have a higher mobility, while the paramolecules are characterized by a greater capacity to form complexes. The question of whether the ortho- and paracomponents of water exist and spectroscopically show up in the liquid phase is still open. Also, it is still unclear whether there is any selectivity in intermolecular interactions in liquids on the basis of ortho- and paramodifications of molecules.

In this report, we review the recent experiments carried out in the Laboratory of Applied Hydrophysics of the Wave Research Center at the Prokhorov General Physics Institute, RAS. In these experiments, with the aid of four-photon scattering, we observed the spectra of low-frequency librations (torsional vibrations) and rotations of molecules in various liquids in the 0 – 3 THz range. The liquids were selected on the basis of the hypothesis that the contribution of rotational resonances to the four-photon scattering signal increases as the intermolecular interaction becomes weaker. Furthermore, a systematic study was made of the four-photon scattering spectra in the 0 – 100 cm^{-1} range in a macroscopic volume of aqueous solutions of the α-chymotrypsin protein. This range was selected because it contains the Mandel'shtam – Brillouin resonances, the Rayleigh wing, and the RS resonances that correspond to the vibrational and orientation motion of molecular protein fragments and the intrinsic low-frequency spectra of the ortho- and para-spin isomers of H_2O molecules in the liquid phase.

2. Experiment

Experiments were carried out on the facility described at length elsewhere [17]. Two counterpropagating waves $\mathbf{E}^{(1)}$ and $\mathbf{E}^{(2)}$ with frequencies ω_1 and ω_2 traveled in a cell filled with a liquid. The entrance and exit cell windows were made of fused quartz and had only an insignificant effect on the state of polarization of transmitted radiation. The wave $\mathbf{E}^{(1)}$ (the second harmonic radiation of an Nd:YAG laser operating in a single longitudinal mode, the intensity typically equal to ~ 60 MW cm^{-2}) was circularly polarized. The frequency-tunable $\mathbf{E}^{(2)}$ wave with the intensity ~ 10 MW cm^{-2} was linearly polarized. With the polarization states of the interacting waves selected in this way [9, 10], the nonresonance contribution made by the electron subsystem of the medium to the signal determined by nonlinear source (1) can be substantially suppressed by tuning the polarization selector.

Because the unit polarization vectors of the signal wave at the frequency ω_s and of the wave $\mathbf{E}^{(2)}$ are noncollinear and their traveling directions coincide, the four-photon scattering signal was selected by a Glan prism. The width of the spectrometer instrumental function (~ 0.1 cm^{-1}) and the spectral range (from -1200 to 300 cm^{-1}) were determined by the output characteristics of a laser utilizing an ethanol solution of 'Coumarin-500' dye. This laser (the $\mathbf{E}^{(2)}$ wave) was pumped by the third harmonic of Nd:YAG-laser radiation and was program-tunable in frequency. For each value of the frequency ω_2, the signal was averaged over 10 – 30 readings; then, the laser frequency was automatically tuned at intervals ~ 0.119 cm^{-1}. The zero-frequency detuning was referenced as accurate to 0.02 cm^{-1} using the Mandel'shtam – Brillouin resonances, and the subsequent wavelength tuning was verified using the modes of a Fabry – Perot interferometer with a 7 mm base (with the free spectral range equal to ~ 1.4 cm^{-1}).

Measurements were made in 'Milli-Q' water (H_2O), heavy water (D_2O), 30% and 5% aqueous solutions of hydrogen peroxide (H_2O_2) and α-chymotrypsin (concentrations of 10 and 17 mg ml^{-1}), and carbon tetrachloride (CCl_4) in the spectral range between -100 and 100 cm^{-1}. Here, the negative detuning pertains to the scattering signal in the anti-Stokes region. The 'Milli-Q' water (reagent quality, type I, specific resistance 18.2 MΩ cm, residual impurity under 20 μg l^{-1}) was produced in the 'Millipore' facility immediately prior to the experiment. The D_2O, H_2O_2, and CCl_4 samples were commercial OSCh (ultrapure) and KhCh (chemically pure) class reagents. Among the above media, the strongest intermolecular interaction due to the hydrogen bond is observed in H_2O and the weakest in CCl_4, whose molecules are considered to be spherical tops [18].

3. Experimental results

Figure 1 shows the four-photon scattering spectra in the spectral range from -8 to 8 cm^{-1} recorded under similar experimental conditions in CCl_4, H_2O, and the aqueous solution of hydrogen peroxide. Each of the spectra shows a line doublet (indicated by arrows) in the ± 0.5 cm^{-1} spectral range arising from the scattering by acoustic phonons (the Mandel'shtam – Brillouin resonances) and several narrow

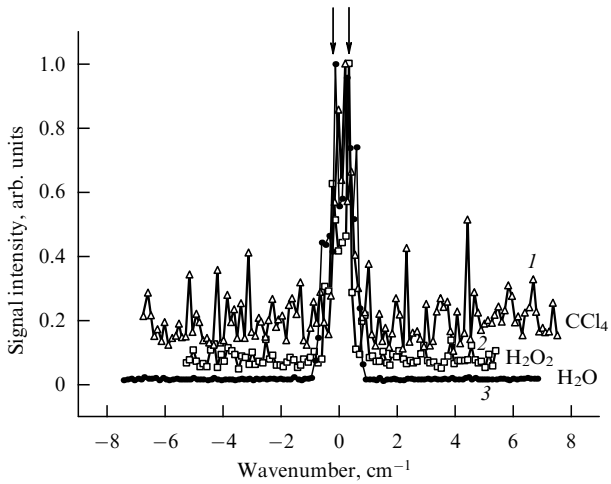

Figure 1. Four-photon scattering spectra normalized to the corresponding peaks of the signals due to the Mandel'shtam – Brillouin resonances in the following liquids: CCl_4 (curve *1*), H_2O_2 (curve *2*), and H_2O (curve *3*) in the spectral range between -8 and 8 cm^{-1}. In the spectral range ± 0.5 cm^{-1}, each of the spectra shows a line doublet (indicated by arrows) arising from the scattering by acoustic phonons.

resonances in the region > 1 cm^{-1}, which are comparable in width to the spectrometer instrumental function. For convenience of comparison, the spectra plotted in Fig. 1 are normalized to the corresponding peaks of the signals of the four-photon scattering due to the Mandel'shtam – Brillouin resonances, whose cross section in CCl_4 is approximately 5 times greater than in water [10]. This circumstance is responsible for the corresponding apparent lowering of resonance amplitudes in CCl_4 (see Fig. 1). One can see from the spectra that the greatest contribution to the scattering signal outside the ± 1 cm^{-1} range is in CCl_4 and the smallest is in H_2O. The increase in the contribution of the narrow resonances to the spectrum of the aqueous solution of H_2O_2 in comparison with the contribution of these resonances to the spectrum of water (H_2O) is attributable to the weakening of intermolecular interaction in hydrogen peroxide. It is well known that the H_2O_2 molecules form two hydrogen bonds with H_2O, while the water molecules form four bonds [1, 2].

Figure 2a shows a part of the four-photon scattering spectrum in the region $\omega_1 - \omega_2 > 0$ for liquid CCl_4 (curve *1*) on which the part of the same spectrum in the anti-Stokes region $\omega_1 - \omega_2 < 0$ (curve *2*) is superimposed. The frequencies of the rotational spectrum of free $^{12}C^{35}Cl_4$ molecules (the fraction of these molecules in CCl_4 is equal to $\sim 32.54\%$ [19]) obtained by *ab initio* calculations are indicated by vertical lines. The calculation was performed neglecting the isotopic substitution of Cl and C atoms [19]. Figure 2a suggests that the spectral positions of the resonances for a positive (curve *1*) and negative (curve *2*) detuning agree satisfactorily (to within the instrumental function) with the calculated ones for the rotational spectrum of the CCl_4 gas. Extra lines in the experimental spectrum are supposedly due to the occurrence of resonances of the CCl_4 molecules with a different isotopic composition. Approximating the spectrum in Fig. 2a by the function $0.267 \exp\left[(\omega_1 - \omega_2)/0.647\right] + 0.12$, which has the width ~ 1.3 cm^{-1} at the level of e^{-1}, permits estimating the time of orientational relaxation due to low-frequency molecular librations as ~ 25 ps. This value coincides with the characteristic time (10 – 50 ps) of dielectric relaxation of organic liquids [20].

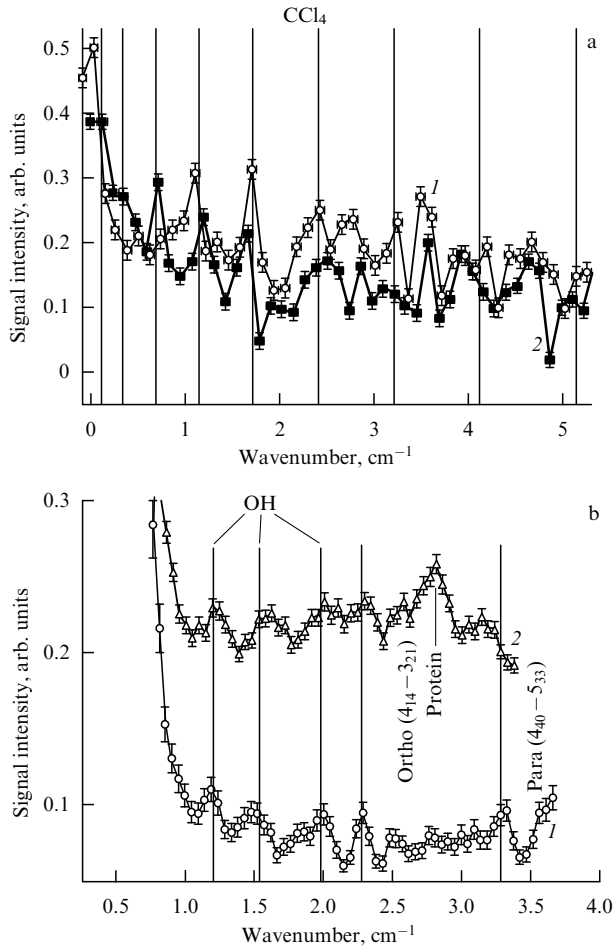

Figure 2. (a) Part of the four-photon scattering spectrum in the region $\omega_1 - \omega_2 > 0$ for liquid CCl_4 (curve *1*) on which the part of the same spectrum in the region $\omega_1 - \omega_2 < 0$ (curve *2*) is superimposed. The vertical lines indicate the frequencies of the rotational RS spectrum of the CCl_4 molecule calculated *ab initio*. (b) Spectra of the four-photon scattering in water (curve *1*) and protein solution (curve *2*). The vertical lines indicate the resonance frequencies of the OH and H_2O molecules.

Figure 2b shows fragments of the spectra of H_2O (curve *1*) and aqueous solution of α-chymotrypsin (curve *2*) at the concentration 10 mg ml^{-1}. Water resonances are indicated by vertical lines. The α-chymotrypsin line (2.8 cm^{-1}) is labeled. The 2.26 cm^{-1} and 3.21 cm^{-1} water resonances are attributed, with an accuracy of the instrumental function, to the rotational transitions $4_{14} - 3_{21}$ and $5_{33} - 4_{40}$ of the ground vibrational state of the ortho- and para-spin isomers of water molecules, respectively [14]. From spectrum *2* (Fig. 2b), it is clear that the 3.21 cm^{-1} line of the paraisomer of water is absent from the solution of protein. This fact is supposedly due to the selective damping of free rotation and the bonding of water paraisomer molecules by protein molecules, as in the case where the vapor is passed above a rough surface [16].

A series of experiments was conducted in which the four-photon scattering spectrum was recorded under similar conditions in heavy (D_2O) and light (H_2O) water and their 50% mixture in the 0 – 100 cm^{-1} (0 – 3 THz) range. The aim of these experiments was to compare the rotational resonance frequencies observed for the D_2O and H_2O molecules in the liquid phase with the values tabulated in Refs [14, 21]. As an example, Fig. 3a shows the spectrum of the $H_2O - D_2O$ mixture (1 : 1) in the 0 – 50 cm^{-1} range smoothed over three

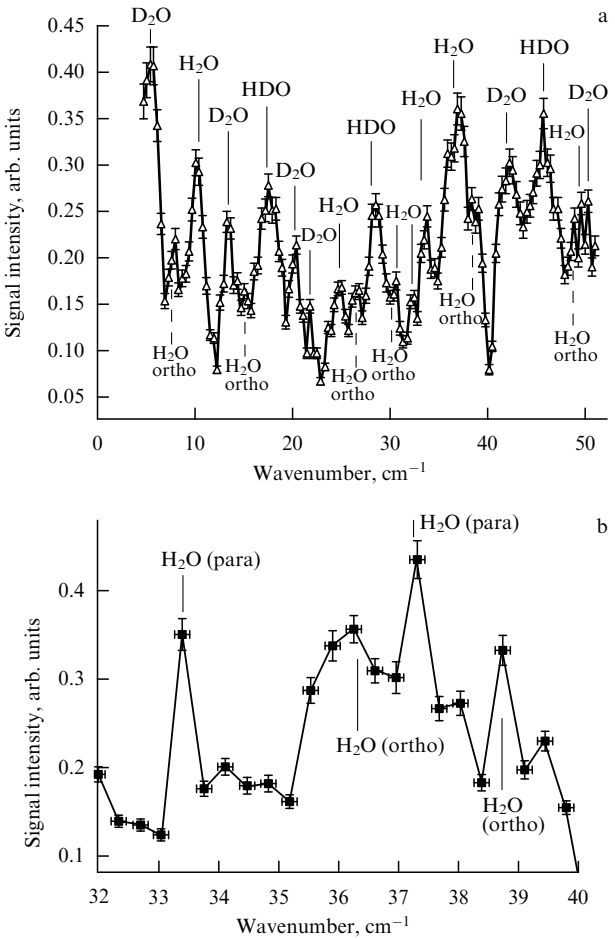

Figure 3. (a) Four-photon scattering spectrum in the 50 : 50 mixture of heavy (D_2O) and light (H_2O) water. (b) Fragment of the spectrum shown in Fig. 3a in the region of the 36.6 and 37.13 cm^{-1} line doublet arising from transitions in the ortho- and para-spin isomers of water molecules.

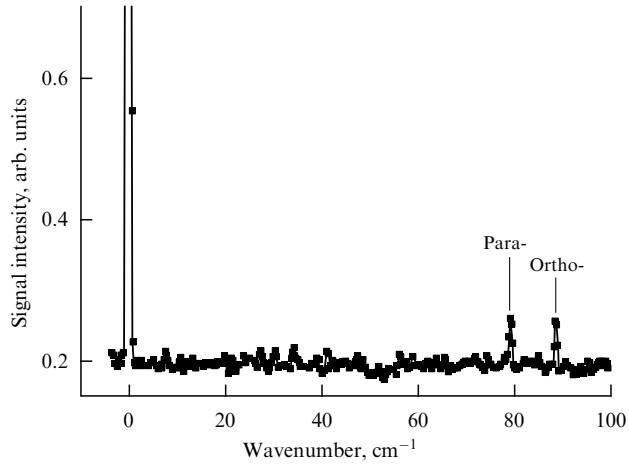

Figure 4. Panoramic four-photon scattering spectrum in 'Milli-Q' water in the 0 – 100 cm^{-1} range.

experimental points to simplify the comparison with the tabular data. The rotational transition resonances pertaining, according to the data in Refs [14, 21, 22], to the spectra of free rotation of the D_2O, H_2O, and HDO molecules, are indicated by labels. The dashed indications pertain to the most intense lines of the rotational transitions of the water ortho-spin isomer. Figure 3b gives the 32 – 40 cm^{-1} portion of the spectrum, where four lines of the ortho- and paramolecules of H_2O show up [14]. Interestingly, the ratio between the line amplitudes in these spectra may differ from their ratio in the IR absorption spectrum because in the four-photon scattering they are proportional to $(1 - 3\rho)$, where ρ is the degree of depolarization of the corresponding RS-active resonances [10]. It is pertinent to note that the rotational resonances of the three types of molecules (D_2O, H_2O, and HDO) are observed in the four-photon scattering spectra of the 50% liquid $D_2O - H_2O$ mixture without noticeable frequency shifts.

The last-mentioned circumstance calls for elucidation. The issue of the effect of intermolecular interaction on the RS and IR absorption resonance frequency shifts in transforming from a gas to a liquid was intensively investigated in the middle of the 20th century (see, e.g., monograph [23]). For different interaction types, this shift was shown to range from $\sim 0.2\%$ to $\sim 0.001\%$ of the corresponding transition frequencies. Clearly, for molecular vibration frequencies, which lie in the 1000 – 4000 cm^{-1} range, this correction is appreciable in magnitude. But for the rotational resonances in the < 100 cm^{-1} region observed in our experiments, this shift should be of the order of 0.2 cm^{-1}, i.e., comparable to the width of the spectrometer instrumental function.

A series of experiments was conducted to reveal the effect of protein molecules on the ortho- and para-spin isomers of a molecule in the liquid phase. Figure 4 shows the spectrum of deionized 'Milli-Q' water in the 0 – 100 cm^{-1} range. The 79.8 cm^{-1} (paramolecule) and 88.1 cm^{-1} (orthomolecule) resonances [14, 24], the strongest in the above range, are clearly visible in the spectrum and are indicated by the corresponding labels. These resonances pertain to the $(4_{04} - 3_{13})$ and $(4_{14} - 3_{03})$ rotational transitions of the ground vibrational state of the para- and ortho-spin isomers of water molecules, respectively. Specified in parentheses are the rotational quantum numbers J, K_a, and K_c of the initial and final levels for the corresponding transitions of the main water isotope borrowed from the HITRAN (high-resolution transmission molecular absorption) database [14]. We emphasize that the majority of the rest lines of the water vapor absorption spectrum in the 0 – 100 cm^{-1} range are formed by superposition of close resonances of the ortho- and paraisomers of water [14] and are therefore less suitable for solving the problem formulated above.

Figure 5 shows the fragment of the water spectrum in the 73 – 91 cm^{-1} frequency detuning range. Using the HITRAN database [14], all resonances observed in the spectrum can be ascribed to the rotational transitions of the lower vibrational state 74.1 cm^{-1} $(5_{14} - 5_{05})$, 78.2 cm^{-1} $(7_{25} - 7_{16})$, and 88.1 cm^{-1} $(4_{14} - 3_{03})$ of orthomodifications and 79.8 cm^{-1} $(4_{04} - 3_{13})$, 85.0 cm^{-1} $(9_{46} - 8_{53})$, and 90.8 cm^{-1} $(12_{75} - 11_{84})$ of paramodifications of the main isotope of the H_2O molecule. The resonances of ortho- and paramolecules of water are indicated.

Figure 6 shows the fragments of the spectra of the α-chymotrypsin protein solution (for the concentration 17 mg ml^{-1}) and the 'Milli-Q' water in the 73 – 91 cm^{-1} range. For convenience of comparison, the water spectrum is extended eight-fold along the vertical axis. The rotational resonances of the ortho- and paraisomers of the water molecule are indicated respectively by thin and bold arrows. These resonances were ascribed to the frequencies using the data in Ref. [14]. The following rotational transitions of the

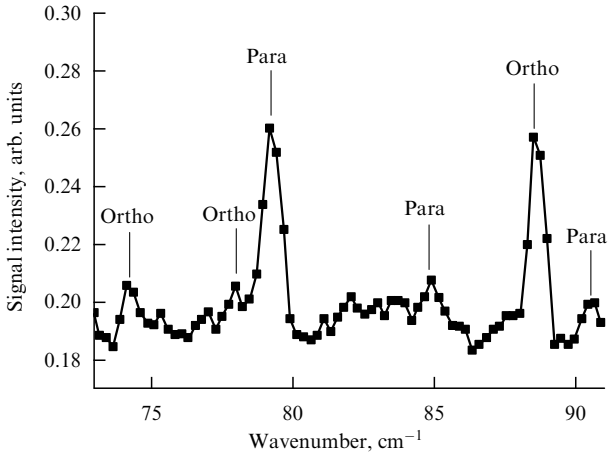

Figure 5. Fragment of the 'Milli-Q' water spectrum in the 73–91 cm^{-1} frequency detuning range. Indicated are the resonances of ortho- and paramolecules of H_2O.

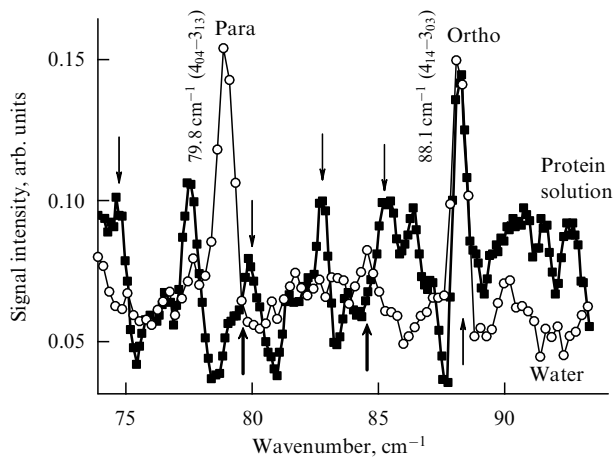

Figure 6. Fragments of the spectra of an aqueous solution of α-chymotrypsin (for the concentration 17 mg ml^{-1}) and 'Milli-Q' water in the 73–91 cm^{-1} range. The rotational resonances of ortho- and paraisomers of the molecule are indicated respectively by thin and bold arrows.

orthomodification of water are clearly identified in Fig. 6: 73.3 cm^{-1} ($3_{30}-3_{21}$), 74.1 cm^{-1} ($5_{14}-5_{05}$), 77.3 cm^{-1} ($9_{45}-9_{36}$), 81.0 cm^{-1} ($9_{36}-9_{27}$), 82.15 cm^{-1} ($4_{32}-4_{23}$), 83.5 cm^{-1} ($10_{47}-9_{54}$), 85.6 cm^{-1} ($7_{34}-7_{25}$), 86.4 cm^{-1} ($4_{23}-4_{14}$), and 88.1 cm^{-1} ($4_{14}-3_{03}$). We note that the 88.1 cm^{-1} ($4_{14}-3_{03}$) line of the orthoisomer remained dominant in the spectrum upon dissolving α-chymotrypsin in the water, while the 79.8 cm^{-1} ($4_{04}-3_{13}$) line of the paraisomer turned out to be strongly suppressed, which points to the selectivity of the interaction of protein molecules with the ortho- and paraisomers of H_2O.

4. Discussion

The experiments conducted in our work show that the spectra of four-photon laser radiation scattering in several liquids (CCl_4, H_2O, D_2O, H_2O_2) exhibit narrow resonances, which coincide in frequency, to within the width of the spectrometer instrumental function, with the rotational transitions of the ground electronic and vibrational states of the corresponding molecules. In this case, separately identified in the spectrum of liquid water are the lines pertaining to orthomodifications and paramodifications of the main isotope of the H_2O molecule. The same lines are observed to be almost ten times stronger in the spectra of the aqueous solution of α-chymotrypsin. This fact testifies to the increase in the fraction of free water molecules in the protein solution.

The increase in the rotational spectrum contribution to the signal of four-photon scattering in the protein solution in comparison with the similar contribution in the case of H_2O is attributable to the formation of a weak hydrogen bond between the water and protein molecules. The experimentally observed suppression of the rotational lines chiefly of the paraisomer of water molecules in the protein solution indicates the selective hydration of biological macromolecules by the paraisomers of water molecules. We note that the selective sorption from the gas phase of the paraisomers of water molecules in passing above the surface of DNA, lysozyme, and collagen samples was previously observed in Ref. [25].

Arguably, the free motion of molecules in liquids emerges at the instant the force of intermolecular interaction (which is strongest in water due to the hydrogen bond) vanishes for some molecules as a result of density fluctuations in the thermal molecular motion. This force rapidly changes with the intermolecular distance because, for instance, for the Lenard-Jones potential

$$U(r) = -\frac{a}{r^6} + \frac{b}{r^{12}}\,, \qquad (2)$$

the attractive force decreases as $\sim r^{-7}$. As a result, individual molecules acquire the capacity for free motion, to essentially become gas molecules.

The existence of a rotational structure in four-photon scattering spectra enables one to spectrally separate the fast and slow motion of molecules and estimate the relative fraction of their contributions. This possibility is nonexistent in RS and nuclear magnetic resonance, where all kinds of orientational motion make contributions to the broadening of the resonances recorded [3, 4, 12, 13]. The spectra of liquids obtained in our experiments are indicative of an appreciable number of free molecules that do not participate in the formation of associated complexes at the instant of probing.

Because every resonance whose contribution to the four-photon spectrum is proportional to $(\mathrm{Im}\,\chi^{(3)})^2$ [see relation (1)] is reflective of some mechanism of energy dissipation in the medium (hypersonic waves, librations, free molecular motion), the curves in Figs 1–6 reproduce the absorption spectra of the media under investigation in the terahertz and subterahertz frequency ranges. The fact that these spectra are not continuous permits finding the frequencies at which different liquids, in particular water, exhibit a higher or lower level of microwave radiation absorption. This circumstance allows reconsidering the numerous facts surrounding the selective action of microwave radiation on living organisms [11]. In this case, the high Q value of resonances with a linewidth no greater than the width of the instrumental function (~ 0.2 cm^{-1}) suggests the feasibility of their saturation under pulsed exposure to resonance radiation. The spectral separation of the contribution of slow and fast motion to the orientational molecular relaxation opens up additional possibilities for the study of molecular interactions in the physics of liquids [26].

It is beyond the scope of this report to discuss the results of a series of works on the measurement of the fractal dimension

of polymers, molecular associates, and biological macromolecules in a liquid using four-photon low-frequency scattering spectra. Rapid strides are being made in this area [27, 28]. In our experiments [29, 30], a study was made of the spectral response of coherent four-photon laser-radiation Rayleigh-wing scattering, which was used to calculate the phonon state density dispersion. The phonon state density dispersion is known [27, 28] to be the main source of information in the study of the fractal dimensionality of condensed media. We have elaborated an approach offering several advantages over traditional techniques of low-angle scattering of thermal neutrons and X-rays, as well as over spontaneous Rayleigh-wing scattering of light. These advantages include the relative simplicity of the experiment; a high level of the desired signal in comparison with the signal level in the case of spontaneous Rayleigh-wing scattering; a high energy (spectral) resolution, especially in comparison with the resolution in neutron diffraction analysis; and the possibility, due to the coherent nature of the scattering, of extracting the components arising from the slow reorientations of large molecular fragments in the recorded signal. We emphasize that the last-mentioned factor is nonexistent in the traditional approaches to the measurement of the fractal dimension.

Of special interest is the successful recording of low-frequency spectra of aqueous solutions of proteins in water, i.e., in the medium natural for biological molecules. It is noteworthy that the solution of the α-chymotrypsin protein was accompanied by the manifestation of the selective property to form complexes only with the paraisomer of water molecules. Recording the capacity for spin-selective adsorption of proteins in an aqueous solution allows developing radically new approaches to the investigation of the properties of the membrane aquaporin protein, which is responsible for the transmission of a consecutive chain of single water molecules into a cell. Its discovery was rewarded with a Nobel Prize [31].

The practical significance of the low-frequency resonances discovered in water is evident. Undoubtedly, the most interesting in this case is the study of the influence of microwave radiation and the means of mobile communication with the frequency ~ 1.8 GHz on biological subjects. This stems from the fact that water and hydroxyl molecules have rotational resonances at the frequencies 0.072 cm^{-1} (2.16 GHz) and 0.057 cm^{-1} (1.72 GHz), which are close to the frequencies of microwave devices and the radiation of space masers utilizing these molecules [32].

5. Conclusion

For the first time, with the aid of coherent four-photon scattering, it has been possible to discover narrow resonances in several liquids (CCl_4, H_2O, D_2O, H_2O_2) in the submillimeter wavelength range. These resonances coincide in frequency, to within the width of the spectrometer instrumental function, with the rotational transitions of the ground electronic and vibrational states of the corresponding molecules. The water spectra clearly exhibit resonances pertaining to the lines of the ortho- and paraisomers of the main isotope of H_2O molecules in the gas phase.

The resonance contribution of coherent librations to the four-photon scattering signal significantly increases in passing from water to a protein solution. The mechanism of this effect is not yet completely clear. However, it is conceivable that the presence of protein molecules in the solution is responsible for the disruption of the initial topology of the hydrogen bond network in water, increasing the concentration of weakly bound molecules.

The protein molecule in solution was found to actively interact with the paramodification of the H_2O molecule. This effect permits interpreting the selectivity of microwave radiation action on biological subjects [11] and offers prospects for developing a new class of laser biotechnologies.

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Nuclear explosions as a probing tool for high-intensity processes and extreme states of matter: some applications of results

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1. Introduction

Nuclear explosions, along with releasing massive amounts of energy, involve high initial density and intense fluxes of neutron, gamma, X-ray, and electromagnetic radiation, as well as intense radiation, fluid dynamic, electromagnetic, and seismic processes — all this providing a way to study phenomena previously beyond our reach. One example is the self-similarity property of the shock wave flow [1–3] — an important feature of the evolution of high-power explosions in gases, which was already discovered when the first air nuclear explosions were being prepared and carried out and which was later observed and used in laboratory experiments (for example, in the energy diagnostics of high-intensity laser pulses [4]) and in interpreting explosion phenomena in astrophysics.

For explosions of a sufficiently high intensity, assuming a power-law temperature dependence of the heat conductivity, the self-similarity property is also found at an earlier, thermal stage of energy transfer [5, 6]. Such processes occur when radiation and matter have already thermalized but gas-dynamic energy transfer is still negligibly small. The modes of behavior at this stage also carry information about the nonlinear heat conduction properties of the matter involved. Preceding the thermal stage is that of the nonequilibrium propagation of radiation (which was analyzed in [7] for air explosions). The explosion evolution in the air involves a number of gasdynamic, thermal, and optical processes (see monograph [6] for a review), many of which were invoked to justify and apply the methods with which the energy of air explosions was measured.

In Russia, the transition to underground explosions in 1964 posed new problems but also improved opportunities for physical research in the field. Although they share some similar stages with their air counterparts, underground explosions are different in both scale and the underlying physics.

During the period of air tests, only one on-site experiment — the physics experiment of 1957 — was successfully carried out using high-intensity processes for research purposes [8]. With underground explosions, a similar research was begun in our institute in the first on-site experiments and continued until the last test in 1989. The present author has been privileged to have participated in setting up, performing, and interpreting most of these experiments.

This research stimulated efforts to develop theoretical models and mathematical software tools for describing extreme states of matter and high-intensity pulsed processes — work that was paralleled by special-purpose on-site experiments designed to test models and their mathematical realization and to accumulate experimental data. In this way, a science technology including theoretical work, mathematical simulation, and associated experimentation tools and facilities was developed and subsequently further improved, adapted, and applied to new classes of phenomena, such as the interaction of high-power laser beams with matter, the acoustic collapse of microbubbles, high-intensity magnetohydrodynamic processes, and explosion phenomena in astrophysics.

In this talk, the use of explosions as a tool for exploring high-intensity processes and probing the properties of the media involved are briefly described, together with advances in developing theoretical models, and two examples are given to show how other fields can profit from the science technology developed. The first example presents some results on how the threat of small bodies from space (asteroids or comets) hitting Earth can be prevented by using explosions to change their trajectories or to disperse them. The second example discusses a mechanism that governs the propagation of a burning wave on the surface of an accreting neutron star and explains the front modulation of first-type X-ray bursts in low-mass binary systems.

2. General characteristics of explosions and the methodology for their study

The most important features of nuclear explosions are that they are highly localized (typically within dozens of centimeters to several meters) and release huge amounts of energy at a very fast rate (time scale ranging from a few nanoseconds to fractions of a millisecond), with the mass of energy-releasing regions ranging from a few to hundreds of kilograms. The amount of energy released in a nuclear reaction can be larger than ~ 1 MeV per nucleon. Although the energy density averaged over the masses of the energy-releasing regions is lower than that, the matter can reach the temperature 10 keV or more as the energy of the reaction products is transferred to the surrounding atoms. The total explosion energy E_0 varies widely, from fractions of a kiloton to several megatons TNT equivalent ($1\ \text{kt} = 4.18 \times 10^{12}$ J). Because of the high initial temperature, the transfer of the released energy into the surrounding medium first occurs due to radiation. In parallel with this, nonequilibrium neutron and gamma-ray transfer processes operate, which can hinder but can also facilitate doing experiments of high informative value. We note that despite the high energy release density, the energy-releasing regions and the explosive device and its operation supporting system have finite sizes, often comparable to the linear scale of the processes under study (or in use) and must therefore be taken into account in describing the phenomenon.

Underground explosions were carried out in horizontal galleries and vertical holes (see, e.g., Ref. [9]), the burial depth of the charge varying from hundreds of meters to several kilometers, and a specially developed technology ensured the radiation and seismic safety of the experiment. The measurement program was varied on an experiment-to-experiment basis. A special concern was that the conditions at the location of the charge be optimized for conducting the study. While the horizontal scenario is more convenient in this respect, it involves constructing underground workings, drilling holes for instruments, mounting detectors, and