

LETTERS TO THE EDITORS

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Once again, on the observation of molecular rotational spectra in condensed media

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Abstract. Our reply to critical comments by A F Krupnov and M Yu Tretyakov (*Usp. Fiz. Nauk* 179 1363 (2009) [*Phys. Usp.* 52 (12) 1273 (2009)]) and M A Bol'shov, A A Makarov, and V P Mironenko (*Usp. Fiz. Nauk* 179 1368 (2009) [*Phys. Usp.* 52 (12) 1279 (2009)]) on a paper by A F Bunkin, A A Nurmatov, and S M Pershin (*Usp. Fiz. Nauk* 176 883 (2006) [*Phys. Usp.* 49 855 (2006)]).

In their letters to the Editors of *Uspekhi Fizicheskikh Nauk*, M A Bol'shov, A A Makarov, and V P Mironenko, and A F Krupnov and M Yu Tretyakov comment on our paper [1] published in *Usp. Fiz. Nauk* in 2006.

We point out that Ref. [1] outlined the experimental results on Raman scattering (RS) spectroscopy of coherent four-photon laser scattering in condensed media using a facility which had theretofore been repeatedly calibrated by well-known RS resonances in different liquids, gases, and solids. That is why we do not cast doubt on the existence of the narrow resonances specified in Ref. [1] and do not question the spectroscopic parameters (e.g., the widths of the resonances and their frequency positions) given in Ref. [1]. The data of previously unperformed experiments may be interpreted in different ways; in 2005–2006 we came up with the interpretation set forth in Ref. [1].

It is hard to argue against the comments made by A F Krupnov and M Yu Tretyakov [2], because the authors of that letter apparently do not understand the dissimilarity of their customary microwave absorption spectroscopy from four-photon RS spectroscopy whose signal is determined by the cubic nonlinear susceptibility tensor $\chi^{(3)}$, as is clearly stated in Ref. [1]. This misunderstanding follows, for instance, from their remark: "This was ... a radiation interference signal — an ordinary occurrence for this wavelength range" [2, p. 1273]. In our experiments, all the radiation in use lies in the visible spectral range. This is the reason why the remarks pertaining to infrared absorption spectroscopy cannot apply to the four-photon scattering spectroscopy, as also stated in the comment made by M A Bol'shov, A A Makarov, and V P Mironenko [3].

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We now turn to the essence of the comments.

(1) We begin with the title of Ref. [1]. Our experimental facility [1] enables obtaining in the framework of one approach the spectra of liquids, gases, and solids in the frequency range from 0.1 cm^{-1} to 700 cm^{-1}. That is why the resonances observable in this range, which encompasses translational motion, intermolecular oscillations, rotations (including hindered rotation), and librations, are hard to describe with a single word. In some of our papers this range was termed 'low-frequency'. However, this definition cannot be regarded as being felicitous, either, because this range is low-frequency for the optical spectrum and super-high-frequency for radio-frequency spectroscopy. And so in this case we resorted to the terminology accepted in the English-language literature, in which the entire 60–900 cm^{-1} range is frequently referred to as the 'librations and hindered rotations' or 'librations and hindered translations' range (see, for instance, Eisenberg and Kauzmann [4]).

(2) Our CCl_4 measurements were made in a chemically pure liquid with a natural isotopic composition, i.e., for the isotopic percentages 32.54%, 42.17%, 20.50%, 4.43%, and 0.36%, with $^{12}C^{35}Cl_4$ accounting for only 32.54%. That is why the equidistant RS spectrum referred to in the critical comments is out of the question in principle. The rotational RS-spectrum frequencies of different CCl_4 molecules were calculated by our colleagues, who are professionally engaged in this activity, with the inclusion of the isotopic composition. These frequencies coincided with the resonances of the four-photon scattering spectrum recorded in our experiments, which was set forth in Ref. [1].

(3) In the 0.1– 300 cm^{-1} frequency range investigated in our experiments, no less than 500 spectral lines are observable in distilled water and in the aqueous solutions of different biological molecules and carbon nanotubes. It seems likely that some of these lines were incorrectly interpreted in Ref. [1]. However, exhaustive interpretation is hardly attainable at the present time, because the data of Ref. [5], which are mentioned by M A Bol'shov et al. [3], are evidently at variance with the data of G Avila et al. [6] (to make sure that this is so, it would suffice to compare Table 5 from Ref. [6] with the table from Supplement 3 in Ref. [5]). Significant distinctions are also encountered in different versions of the HITRAN Database. We therefore employed HITRAN as the most complete database as regards rotational transitions in the H_2O molecule at that moment. In the course of subsequent experiments, it was found that distilled water and the aqueous solutions of biopolymers contain appreciable amounts of hydrogen peroxide whose molecules possess a complex spectrum in the frequency range specified above. In 2004–2006, we could not even imagine that.

Unfortunately, the authors of the comments missed the most essential thing in our paper [1]: proposed and experimentally realized in that work for the first time was a new type of spectroscopy, which relies on visible-range lasers whose wavelengths lie in the transparent region of the medium and which enable effecting the terahertz and gigahertz spectroscopy of condensed media, including water, aqueous solutions, and biological objects in the native conditions of a large volume. Precisely therein lies — in this case — the 'advances in the physical sciences' (English translation of the Russian title of the journal 'uspekhi fizicheskikh nauk'). Furthermore, the authors of Ref. [1] came up with an assumption that liquid water and aqueous solutions always contain a certain amount of free H_2O molecules possessing a rotational spectrum. For many years this statement was the object of criticism, whose main proposition was "that cannot be the case, because this can never be the case". However, published in July of 2009 was a paper [7] by 18 authors from the USA, Japan, and several European countries, which showed by way of quasimonochromatic X-ray beam scattering spectroscopy that in liquid water there are also free water molecules and molecular clusters possessing the symmetry of hexagonal ice. Based on our experimental data, we made similar assumptions nearly ten years ago.

And the last remark. In July 2009, a workshop covering the application of terahertz radiation for the diagnostics of biological objects was held in the framework of the International Symposium on Biophotonics. During the workshop, several invited speakers from the USA and Japan discussed the feasibility of using four-photon spectroscopy as a promising line of research, estimated the possible signal-to-noise ratios, and made different predictions. In due course, two of our invited reports were heard. We reported not only the corresponding techniques, but also the extensive experimental data on the four-photon terahertz spectroscopy of biological objects and aqueous solutions. The priority of Russian science in this area was noted in private discussions.

The authors of the present letter recognize that much remains to be done in the specified area. Joined efforts of experts in different fields are called for, including those in classical microwave spectroscopy. We are also aware that in our work, like in any truly novel scientific area, criticism is unavoidable, which is clearly borne out by the present discussion.

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