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Comments on the paper “Coherent four-photon spectroscopy of low-frequency molecular librations in a liquid” by A F Bunkin, A A Nurmatov, and S M Pershin

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Abstract. The results outlined in the paper published in the journal *Uspekhi Fizicheskikh Nauk* (see *Usp. Fiz. Nauk* 176 (8) 883 (2006) [*Phys. Usp.* 49 (8) 855 (2006)]) are analyzed. The interpretation of all the spectra presented is shown to be unsatisfactory, thus compromising the conclusions of the paper.

Uspekhi Fizicheskikh Nauk published the paper “Coherent four-photon spectroscopy of low-frequency molecular librations in a liquid” by A F Bunkin, A A Nurmatov, and S M Pershin [1] based on the results reported by them at the Scientific Session of the Physical Sciences Division of the Russian Academy of Sciences on 29 March 2006.

The main findings of the authors of Ref. [1] were summarized in Section 5, Conclusions: “Therefore, for the first time it has been possible to discover, with the aid of coherent four-photon laser scattering spectroscopy, narrow resonances in several liquids (CCl_4 , H_2O , D_2O , H_2O_2) in the submillimeter wavelength range ($0\text{--}100\text{ cm}^{-1}$). These resonances coincide in frequency, to within the width of spectrometer instrumental function, with the rotational transitions in the ground electronic and vibrational state of the corresponding molecules”.

If confirmed, the results of Bunkin et al. [1] are rather significant, since the generally accepted viewpoint, which relies on numerous experiments, is the one expressed, for instance, in the article “Mikrovolnovaya spektroskopiya” (“Microwave spectroscopy”) written for *Large Encyclopedia Dictionary. Physics*: “Microwave spectroscopy (MS) is an area of radio-frequency spectroscopy operating in the centimeter and millimeter wave range. Most rotational and rotational-inversion molecular spectra, which are impossible to observe in solids and liquids, fall in this range, and therefore MS is frequently identified with the radio-frequency spectroscopy of gases” [2].

Should these results be borne out, they would open up new investigative possibilities and be highly interesting to us who have been involved in microwave spectroscopy for about forty years. However, prior to trying to observe the narrow

lines of rotational molecular transitions in liquids, we decided to scrutinize closely the materials of Ref. [1].

Since the conclusions of the authors of Ref. [1] rely on the data derived from their observed spectra, analysis of the spectra given in Ref. [1] is required. We now turn to a detailed analysis of the spectra of the substances investigated, which are depicted in Figs 2–6 in Ref. [1]. The spectrum of the water molecule is presented the most in the figures and has been best studied to date. We decided to begin with the water molecule spectrum.

In Fig. 2b, the authors of Ref. [1] assign “the 2.26 cm^{-1} and 3.21 cm^{-1} water resonances, with an accuracy of the instrumental function, to the rotational transitions $4_{14}\text{--}3_{21}$ and $5_{33}\text{--}4_{40}$ of the ground vibrational state of the ortho- and para-spin-isomers of water molecules, respectively”, with reference to the well-known HITRAN database [3].

However, in the water spectrum tables the frequencies specified in Ref. [1] are ascribed to the first excited bending (010) vibrational state of the water molecule rather than to the ground (000) state. In the text of paper [1], supposedly due to mistype, the rotational quantum numbers of the initial and final levels of the second (3.21 cm^{-1}) transition are interchanged, i.e., located at this frequency in reality is the $4_{40}\text{--}5_{33}$ transition, and this identification of the 3.21 cm^{-1} transition is indicated in Fig. 2b in Ref. [1]. Neither in the first nor in the second case does the table of frequencies contain lines of the ground (000) vibrational state of H_2^{16}O that are close in frequency. In the spectrum of the ground state of the H_2^{16}O molecule, of the two lines indicated by the authors of Ref. [1], the former ($4_{14}\text{--}3_{21}$) is at a frequency of 12.68 cm^{-1} , the line with quantum numbers $5_{33}\text{--}4_{40}$ is at a frequency of 15.83 cm^{-1} , while the $4_{40}\text{--}5_{33}$ absorption line is absent in the (000)-state. Since Ref. [1] provides the frequency scale for the spectrum presented, errors in frequency are ruled out. The reader may verify the identifications of the lines and their frequencies, referring, for instance, to the tables of experimental energy levels of the water molecule published by Tennyson et al. [4]. It is pertinent to note that the intensities of the specified lines in Fig. 2b from Ref. [1] are equal, while their tabulated intensities differ by nearly an order of magnitude.

The energy of the first excited bending (010) vibrational state of the water molecule is about 1600 cm^{-1} . Considering that at room temperature $k_B T \sim 200\text{ cm}^{-1}$, the Boltzmann population of the vibrational state amounts to only 3.4×10^{-4} , setting the ground state population to unity. If the authors of Ref. [1] observe the lines of an excited state, the ground-state lines shown in the subsequent figures in Ref. [1] should possess no less than a 3000-fold margin in signal-to-

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noise ratio. It is noteworthy that the low intensity of excited-state lines is due not to the low dipole transition moment, or some similar problems, but simply to the small number of such molecules. And they are many in the ground state. We shall revert to this remark when discussing those spectra which contain lines belonging to the ground state of the water molecule.

However, the assumption that Bunkin et al. [1] observed excited-state lines of the water molecule in Fig. 2b is also unsatisfactory. Between the H_2^{16}O lines indicated by the authors of Ref. [1] in Fig. 2b there is, for instance, the $1_{10}-1_{11}$ line of the partly deuterated HDO molecule; for the natural concentration (3×10^{-4}) of the HDO molecules in water, the intensity of this line is higher than the intensities of the specified lines of H_2^{16}O molecules in the excited vibrational state. As can be seen from Fig. 1, in this domain there are several other HDO lines comparable in intensity, for instance, with the line at a frequency of 3.21 cm^{-1} indicated by the authors of Ref. [1]. If the authors of Ref. [1] observe their indicated lines of water molecules in the excited state, they should observe, at the very least, the higher-intensity line of the HDO molecule located in between. The parameters of the three specified lines are collected in Table 1, and the portion of the water vapor spectrum between frequencies of 1 and 3.8 cm^{-1} is diagrammed in Fig. 1. The data were taken from the HITRAN database [3]. They are highly reliable and the authors of Ref. [1] also make use of the database of Ref. [3]. We give the line intensities in $[\text{cm}/\text{molecule}]$ units employed in HITRAN. The line intensities are proportional to the absorption coefficient at the peak of a spectral line, which is commonly used in microwave spectroscopy [5].

Therefore, comparing Fig. 2b from Ref. [1] with the tables of water vapor lines yields unsatisfactory results of the line identifications made by the authors of Ref. [1], and it reveals discordance in the ratios between their line intensities and the absence of HDO lines which should be present in the spectrum lineup.

Figure 3a of Ref. [1] shows a portion of the spectrum of a 1 : 1 mixture of heavy (D_2^{16}O) and light (H_2^{16}O) water in the $0-50 \text{ cm}^{-1}$ frequency range. The authors of Ref. [1] give neither the identifications of the lines nor their frequencies, making impossible direct verification of the authors' central

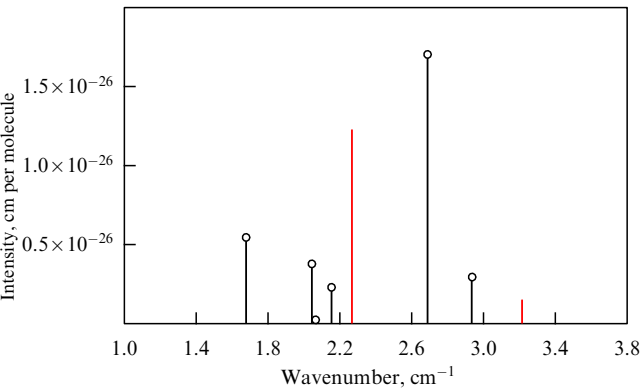


Figure 1. Diagram of the water vapor spectrum in the $1-3.8 \text{ cm}^{-1}$ frequency range calculated using the data of Ref. [3]. One can see the 2.26 - and 3.21-cm^{-1} H_2^{16}O lines indicated by the authors of Ref. [1], as well as several lines of comparable and higher intensity belonging to HDO at the natural concentration (indicated by circles). The lines of other isotopologues of the H_2O molecules, which are also present in water vapor at natural concentration, cannot be seen on this scale.

Table 1.

Molecule	Line $J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$	Vibrational state ($V_1 V_2 V_3$)	Frequen- cy, cm^{-1}	Intensity, cm per molecule (296 K)
H_2^{16}O	$4_{14}-3_{21}$	010	2.26	1.23×10^{-26}
HD^{16}O	$1_{10}-1_{11}$	000	2.69	1.77×10^{-26}
H_2^{16}O	$4_{40}-5_{33}$	010	3.21	0.15×10^{-26}

result that their discovered resonances coincide, to within the width (0.1 cm^{-1}) of the instrumental function of the spectrometer, with the frequencies of rotational transitions in the ground electronic and vibrational states of the corresponding molecules. The belonging to one or other isotopologue of water is indicated only for some of the peaks in Fig. 3a of Ref. [1]. We diagrammed the spectrum for such a mixture, which is depicted in Fig. 2a. In the construction of the diagram we took into account the well-known phenomenon of fast proton exchange, resulting in this mixture in a $0.25:0.25:0.5$ concentration ratio of the D_2^{16}O , H_2^{16}O , and HDO molecules, respectively. A comparison between Fig. 3a of Ref. [1] and our diagram nevertheless allows making some conclusions. The peak intensities in Fig. 3a of Ref. [1] have the same order of magnitude throughout the $0-50 \text{ cm}^{-1}$ frequency range (the highest peak is at a frequency lower than 10 cm^{-1}). In the spectrum diagram of our Fig. 2a, the line intensities increase

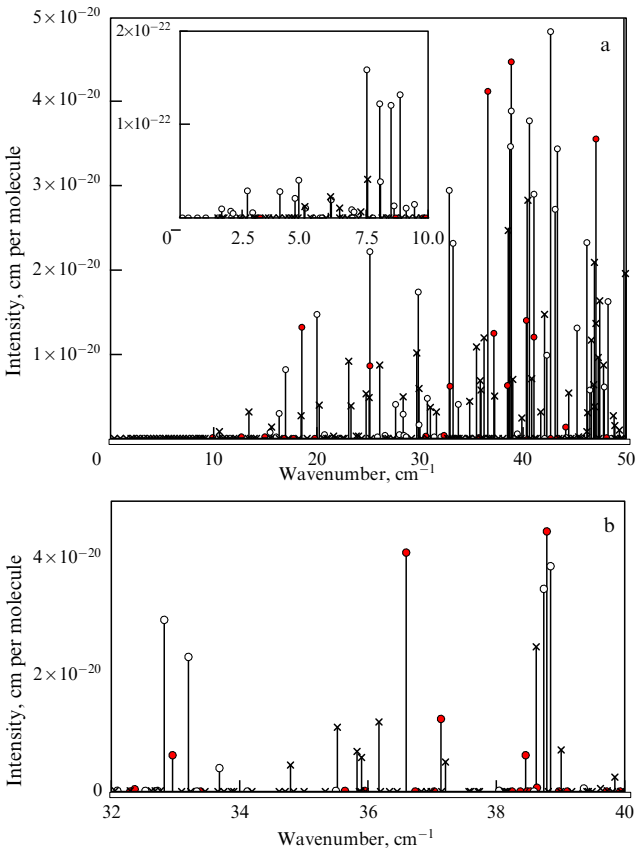


Figure 2. (a) Spectrum diagram in the $0-50 \text{ cm}^{-1}$ frequency range for the vapor produced in the 1 : 1 mixing of heavy and light water. (b) Portion of the diagram in Fig. 2a corresponding to the $32-40 \text{ cm}^{-1}$ frequency range. The D_2^{16}O lines are indicated by white dots, the H_2^{16}O lines by black dots, and the HDO lines by crosses.

rapidly with frequency; the lines with frequencies below 10 cm^{-1} are barely visible in the figure. To make them discernible, we showed a portion of the spectrum in the $0\text{--}10\text{ cm}^{-1}$ frequency range on a highly enlarged scale (by two orders of magnitude) in the inset to Fig. 2a. The independence of the peak intensity from the frequency, which was observed in Ref. [1], is inconsistent with the rotational water spectrum but is not explained by Bunkin et al. [1].

Figure 3b of Ref. [1] presents a portion of the spectrum of Fig. 3a in the $32\text{--}40\text{ cm}^{-1}$ range. In this case, the authors of Ref. [1] specify the frequencies of the “line doublet”: 36.6 and 37.13 cm^{-1} . However, the 36.6-cm^{-1} line of the orthoisomer of the H_2^{16}O molecule, which they mention, is located not near the peak but near the minimum of the signal in the spectrum observed in Ref. [1], while in this frequency range there are no other lines of comparable strength, as is evident from the spectrum diagram of Fig. 2b. In our spectrum diagram, the 37.13-cm^{-1} line intensity of the para isomer of the H_2^{16}O molecule is lower by more than an order of magnitude than the total intensity of the D_2^{16}O , H_2^{16}O , and HDO molecular lines clustering near the frequency of 38.8 cm^{-1} , while the peak at the frequency of 37.1 cm^{-1} in Fig. 3b [1], by contrast, far exceeds in intensity the peak near 38.8 cm^{-1} . The peak at the frequency of 33.4 cm^{-1} , which Bunkin et al. [1] assigned to the water para isomer, is absent in our spectrum diagram, while the three closely spaced lines of HDO and H_2O , which might form a peak at a frequency somewhat lower than 33 cm^{-1} , correspond to a minimum of the spectrum in Fig. 3b taken from Ref. [1]. Therefore, the frequencies and intensities of the peaks in Fig. 3b [1], too, do not correspond to the rotational line spectrum of the mixture of water isotopologues.

The authors of Ref. [1] observe only two lines with an above-noise intensity in the water spectrum in the $0\text{--}100\text{ cm}^{-1}$ range in Fig. 4 [1]. Bunkin et al. [1] state that these two lines are observed — at frequencies of 79.8 cm^{-1} and 88.1 cm^{-1} — as “the strongest resonances in the above range”. We decided to compare Fig. 4 from Ref. [1] with the data taken from Ref. [3]. In the diagram of the water vapor spectrum in the $0\text{--}100\text{ cm}^{-1}$ frequency range shown in our Fig. 3, two lines are really especially prominent, with the difference being that they are at frequencies of 88.1 and 92.5 cm^{-1} . The 79.8-cm^{-1} line is also present in the spectrum, but its intensity is several times lower than that of the 88.1-cm^{-1} line. Furthermore, the diagram also features many other spectral lines comparable in

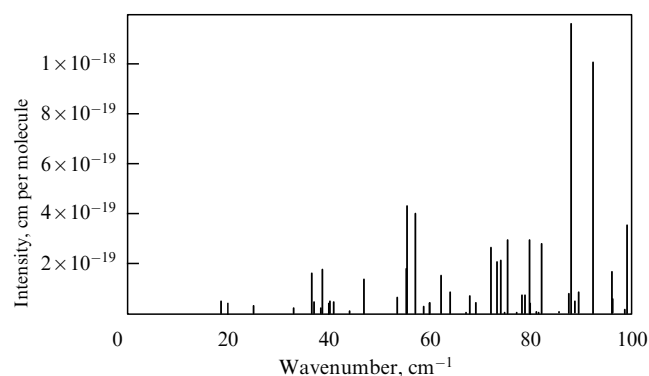


Figure 3. Diagram of the water vapor spectrum in the $0\text{--}100\text{ cm}^{-1}$ frequency interval. The lines at frequencies of 79.8 and 88.1 cm^{-1} indicated by the authors of Ref. [1] can also be found in the diagram. Their intensity ratio and the ratios between their intensities and those of other lines are substantially different from the ratios observed in Ref. [1].

intensity with the two lines specified in Ref. [1]. The authors of Ref. [1] do not explain why they do not observe other lines of virtually the same intensity.

The authors of Ref. [1] identify the observed peaks in Fig. 5 [1] as transitions in the lower vibrational state of H_2^{16}O . For these lines, the signal-to-noise ratio should be several thousand times higher simply due to the higher level population than for excited-state lines shown, for instance, in Fig. 2b (curve 1) of Ref. [1]. Next, more than two orders of magnitude are added by the difference in line frequencies, for the line intensity is proportional to the square of its frequency. Lines also vary in intensity due to the difference in magnitudes of the dipole transition matrix elements. As a result, the ground-state lines indicated in Fig. 5 [1] exceed in intensity the excited-state lines indicated in Fig. 2b by many orders of magnitude, as is evident from the comparison of intensities in Tables 1 and 2, where they are given in the same units. The difference amounting to eight orders of magnitude is highly significant. However, the signal-to-noise ratio for the strongest lines in Fig. 5 is only several times higher than in Fig. 2b. And this is not the only remark.

The first two columns of Table 2 give the data from Fig. 5 taken from the text of Ref. [1]. In the third column we indicated the tabulated intensities. The tabulated intensity values of the lines given in Fig. 5 in Ref. [1] vary by almost six orders of magnitude for different lines, even within the ground vibrational state. However, the intensities of the peaks indicated by the authors of Ref. [1] in the spectrum in Fig. 5 vary only several-fold. This double inconsistency with line intensities, each time by several orders of magnitude, casts doubt on the results presented in Fig. 5 in Ref. [1], to say the least.

In a similar way we analyze Fig. 6 from Ref. [1]. The two left columns in Table 3 also come from the authors of Ref. [1] (the data were taken from the text of Ref. [1]); in what follows, we indicate the intensities and belonging to a vibrational state based on the data taken from Ref. [3]. The authors of Ref. [1] (see, for instance, Section 4) assign all lines in Fig. 6 to “the rotational transitions in the ground electronic and vibrational state of the corresponding molecules”. If one will check this (see Table 3), however, only a portion of the lines indicated by the authors of Ref. [1] are assigned to the ground vibrational state. Figure 6 in Ref. [1] simultaneously shows lines of the ground and excited vibrational states. In the record of the spectrum, their intensities vary only several-fold, while the tabulated intensities of the specified lines diverge by seven orders of magnitude, to take the extreme values. And the identification of one transition is not confirmed. Therefore, the results of considering Fig. 6 from Ref. [1] are also unsatisfactory. So large a discrepancy between the observed and calculated line intensities is inexplicable.

Table 2.

Line $J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$	Frequency, cm^{-1}	Intensity, cm per molecule (296 K)
$5_{14} - 5_{05}$	74.1	0.21×10^{-18}
$7_{25} - 7_{16}$	78.2	0.79×10^{-19}
$4_{14} - 3_{03}$	88.1	0.11×10^{-17}
$4_{04} - 3_{13}$	79.8	0.30×10^{-18}
$9_{46} - 8_{53}$	85.0	0.34×10^{-21}
$12_{75} - 11_{84}$	90.8	0.74×10^{-24}

Table 3.

Line $J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$	Frequency, cm^{-1}	Intensity, cm per molecule (296 K)	Vibrational state
3 ₃₀ –3 ₂₁	73.3	0.21×10^{-18}	000
5 ₁₄ –5 ₀₅	74.1	0.21×10^{-18}	000
9 ₄₅ –9 ₃₆	77.3	0.81×10^{-20}	000
9 ₃₆ –9 ₂₇	81.0	0.11×10^{-19}	000
4 ₃₂ –4 ₂₃	82.15	0.28×10^{-18}	000
10 ₄₇ –9 ₅₄	83.5	0.13×10^{-24}	010
7 ₃₄ –7 ₂₅	85.6	not found*	
4 ₂₃ –4 ₁₄	86.4	0.16×10^{-21}	010
4 ₁₄ –3 ₀₃	88.1	0.11×10^{-17}	000

* There is no 7₃₄–7₂₅ line at the specified frequency. This might conceivably be the 85.63- cm^{-1} 7₃₄–6₄₃ line of the ground state (000) with an intensity of 0.1×10^{-19} , but this changes neither the general picture nor the conclusions.

For OH lines in Fig. 2b taken from Ref. [1], no identification is made. We also found ourselves in a difficulty. If the authors of Ref. [1] imply the neutral OH molecule, it is not clear how it found itself in water. This is not explained in Ref. [1]. It is well known that the molecular OH[–] ion is present in water owing to its partial dissociation. But this is quite a different molecule with a different spectrum. This brings up the question: What kind of spectrum was observed in Ref. [1]? This is not explained by the authors of Ref. [1], either. These are not rotational transitions, which the paper is concerned with: the rotational transitions in OH and OH[–] are much higher in frequency and lie in the terahertz range [6, 7].

Figure 2a in Ref. [1] displays “the rotational RS spectrum of the CCl₄ molecule calculated *ab initio*” as an explanation of the lines observed. “The frequencies of the rotational spectrum of free ¹²C³⁵Cl₄ molecules (the fraction of these molecules in CCl₄ is equal to ~ 32.54%) obtained by *ab initio* calculations are indicated by vertical lines.”

As a spherical top, the ¹²C³⁵Cl₄ molecule in the ground electronic and vibrational state does not possess a rotational spectrum — neither the ordinary infrared spectrum nor the Raman scattering one [8, 9]. The vertical nonequidistant lines in Fig. 2a in Ref. [1] indicate the location of ¹²C³⁵Cl₄ rotational lines expected by the authors. Bunkin et al. [1] supposedly bear in mind some new, previously unknown type of rotational spectrum of CCl₄ but do not explain the gist of matter. Therefore, Fig. 2a [1] with the CCl₄ spectrum also appears as unsatisfactory.

Bunkin et al. [1] arrived at the following conclusions: “Therefore, for the first time it has been possible to discover, with the aid of coherent four-photon laser scattering spectroscopy, narrow resonances in several liquids (CCl₄, H₂O, D₂O, H₂O₂) in the submillimeter wavelength range (0–100 cm^{-1}). These resonances coincide in frequency, to within the width of spectrometer instrumental function, with the rotational transitions in the ground electronic and vibrational states of the corresponding molecules”. However, none of the above-analyzed spectra shown in Figs 2–6 of Ref. [1] confirm these conclusions. The critical remarks about each of these spectra are so serious that the only implication of this analysis is that the authors of Ref. [1] have not proved their statements.

So, what have the authors of Ref. [1] observed? It is likely that some spurious signal was observed in lieu of spectral lines. This was most probably a radiation interference signal — an ordinary occurrence for this wavelength range. This is also confirmed by the fact that the amplitudes of all observed lines, whose highly trustworthy calculated intensities vary by many orders of magnitude, are of the same order of magnitude, including the lines of different molecules observed in one experiment (OH and H₂O), and by the proximity of neighboring peaks. In reality, it is not to be expected that the lines which differ in intensity by many orders of magnitude, or that the different closely spaced lines of different molecules, would be so close in magnitude. As for neighboring interference peaks, they may well be closely spaced and be alike in magnitude. Of course, this is merely one possible explanation.

In this letter we have restricted ourselves to an analysis of the spectra displayed in Ref. [1]. Several other assertions by the authors of Ref. [1] also appear erroneous (or unproven), in particular, about the effect of intermolecular interaction on the frequency shifting of RS and IR absorption resonances in passage from a gas to liquid, about the intensity lowering of the line of the paramodification of H₂O due to “the bonding of water paraisomer molecules by protein molecules”, about the importance of the discovered resonances for applications, etc. However, first of all, the very fact that the authors of Ref. [1] did not detect the transitions they claimed, which follows from the analysis of their spectra, makes discussion of their properties unnecessary. Second, such a discussion would have appreciably increased the length of our letter.

In summary, we also comment on the title of the paper, which does not correspond to the content. The title indicates the observation of libration motions in a liquid. But in the text, the authors of Ref. [1] write that they observed narrow resonances at the frequencies of rotational molecular lines. But libration, which is mentioned in the title of Ref. [1], represents a vibrational motion rather than the rotational one, and the frequencies of these two processes cannot coincide. Indeed, the rotational transition frequencies are determined by the molecular moments of inertia, while the frequencies of libration vibrations are determined by both the molecular moments of inertia and the elastic restoring force which is characterized by the elastic constant of molecular torsional vibrations in the medium. When molecules do not make an oscillation train and their motion is simply a departure from the initial position interrupted by some process, such a motion cannot form narrow resonances, does not have a preferred frequency, and is more likely to correspond to Debye (orientational) absorption.

On analyzing the data of Ref. [1] we decided to put off the application of its results to our investigations.

Our decision to send this letter to the Editors of *Uspekhi Fizicheskikh Nauk* stems from the fact that the paper [1] appeared in a respected scientific journal and its material had been presented at a respectable assembly. The paper by Bunkin et al. [1] apparently was not peer reviewed by a spectroscopist.*

* We consider it necessary to emphasize that the materials of scientific sessions of the Physical Sciences Division of the Russian Academy of Sciences are official materials for the journal *Uspekhi Fizicheskikh Nauk*, which are submitted for publication by the founders of the journal. That is why the manuscripts written on the basis of the reports presented at these sessions are not reviewed by the Editorial Board of *UFN* in advance and are not peer reviewed in *UFN*, unlike all other papers published in the journal. (Editors' note.)

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