# On the observation of molecular rotational spectra in condensed media 

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#### Abstract

This letter was written in connection with the paper by A F Bunkin, A A Nurmatov, and S M Pershin (Usp. Fiz. Nauk 176883 (2006) [Phys. Usp. 49855 (2006)]) and the comments on this paper by A F Krupnov and M Yu Tretyakov (Usp. Fiz. Nauk 1791363 (2009) [Phys. Usp. 52 (12) 1273 (2009)]).


Our comment has been elicited by what, from our standpoint, are the serious mistakes made by Bunkin et al. [1]. Since a physically new manifestation of molecular spectral properties is involved, namely, the rotational structure of the spectra of molecules in a liquid phase, the authors would be expected to furnish a sound reasoning in the interpretation of experimental spectra. In our view, their proposed interpretation is untenable. We shall briefly discuss the main remarks. Like Krupnov and Tretyakov [2], we shall put primary emphasis on the analysis of experimental water spectra and their interpretation.
(1) The authors of Ref. [1] interpret their experimental four-photon scattering spectra as the spectra of water free molecules determined by the cubic nonlinear susceptibility tensor $\chi^{(3)}$. However, to identify the observed lines, recourse was made to the HITRAN Database which contains the lines of linear infrared (IR) absorption defined by the linear susceptibility $\chi^{(1)}$. Four-photon scattering selection rules are the same as for Raman scattering (RS), and therefore the lines arising from transitions between levels of equal parity were primarily bound to be observed. The even and odd levels of water molecules are different in energy, with the consequence that the transition frequencies of linear absorption and RS do not coincide. That is why in the interpretation of their experimental spectra the authors of Ref. [1] should have taken advantage of level wavenumber tables (see, for instance, Bykov et al. [3]), rather than the HITRAN Database for linear absorption. We have analyzed the database of Ref. [3] to find the $\mathrm{H}_{2} \mathrm{O}$ lines, which could be interpreted as fourphoton scattering lines. We found only four such lines: $37.124,77.255,86.42$, and $88.2 \mathrm{~cm}^{-1}$ in the spectral range investigated in Ref. [1]. The second and third lines were interpreted by the authors of Ref. [1] as linear absorption lines from the HITRAN Database. The fourth line coincides, to within the instrumental function, with the $88.1-\mathrm{cm}^{-1}$ line

[^0]from the HITRAN Database. Collected in Table 1 are the lines [3] corresponding to transitions between energy levels of equal symmetry with the appropriate $\Delta J(0, \pm 1, \pm 2)$, which should have been observed but were not observed in Ref. [1]. Apart from the four lines mentioned above, the other lines given in Ref. [1] may not be interpreted as four-wave scattering lines. A discussion and analysis of this situation are completely missing from Ref. [1]. To summarize the aforesaid, it is valid to say that the absence of coincidence of the majority of lines observed in Ref. [1] with RS-active transitions between levels of equal symmetry casts doubt on the interpretation of the molecular spectra as four-photon scattering spectra. If the recorded spectra arise from the linear absorption of water free molecules, the criticism of the results of Ref. [1], well-reasoned in Ref. [2], is absolutely true.
(2) If the authors of Ref. [1] interpret their experimental spectra as the spectra of 'quasifree' molecules in a liquid phase rather than the spectra of completely free ones, the observed linewidth, which is on the order of a fraction of $\mathrm{acm}^{-1}$, is perplexing. As is well known, even in liquid ${ }^{3} \mathrm{He}$, which exhibits the weakest interaction with impurity molecules, the rotational spectrum does not manifest itself, and the linewidths of vibrational transitions are $\geqslant 1 \mathrm{~cm}^{-1}$ [4].

On this basis, it is pertinent to note that the comprehensive and minute comparison of the experimental spectra of Ref. [1] with linear IR absorption spectra, which was made by Krupnov and Tretyakov [2], need not have been undertaken. If Bunkin et al. [1] claim to have interpreted their spectra as four-wave scattering spectra, correlating the intensities and identifying the lines observed in Ref. [1] with those of the HITRAN Database is illegitimate. However, the analysis made by Krupnov and Tretyakov [2] highlighted in full measure the paradoxicality of the results outlined in Ref. [1]: the experimental lines are inconsistent not only with the lines of four-photon scattering by water free molecules, but also with the lines of linear absorption.

We go along with the majority of objections formulated in Ref. [2].
(i) Krupnov and Tretyakov [2] correctly call attention to the strange discrepancy between the intensities of the lines which are interpreted in Ref. [1] as four-wave scattering lines arising from transitions from different molecular vibrationalrotational levels. For any susceptibility, the Boltzmann factor of $\sim 3 \times 10^{-4}$ would be significant simply due to the lowering of the corresponding level populations, so that transitions from an excited vibrational state must be substantially lower in intensity.
(ii) We fully share the doubt expressed by Krupnov and Tretyakov [2] concerning the interpretation of $\mathrm{CCl}_{4}$ and OH molecular spectra. For reasons unknown to us, Bunkin et al. [1] indicated the $\mathrm{CCl}_{4}$ line positions by nonequidistant dotted lines, while the vibrational-rotational lines of the $\mathrm{CCl}_{4}$ molecule ( $\mathrm{T}_{\mathrm{d}}$ symmetry) are equidistant.

Table 1.

| $v, \mathrm{~cm}^{-1}$ | $J^{\prime}$ | $K_{\mathrm{a}}^{\prime}$ | $K_{\text {c }}^{\prime}$ | Parity | $J^{\prime \prime}$ | $K_{a}^{\prime \prime}$ | $K_{\text {c }}^{\prime \prime}$ | Parity | $E^{\prime}, \mathrm{cm}^{-1}$ | $E^{\prime \prime}, \mathrm{cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.86 | 2 | 2 | 1 | - | 3 | 0 | 3 | - | 136.762 | 134.902 |
| 5.742 | 6 | 5 | 1 | - | 8 | 1 | 7 | - | 888.633 | 882.89 |
| 7.341 | 5 | 4 | 2 | $+$ | 6 | 2 | 4 | + | 610.115 | 602.774 |
| 9.489 | 7 | 5 | 3 | - | 8 | 3 | 5 | - | 1059.647 | 1050.158 |
| 9.722 | 3 | 3 | 1 | - | 4 | 1 | 3 | - | 285.219 | 275.497 |
| 11.069 | 7 | 4 | 3 | - | 9 | 0 | 9 | - | 931.237 | 920.169 |
| 13.717 | 6 | 4 | 2 | + | 8 | 0 | 8 | + | 757.78 | 744.064 |
| 14.273 | 7 | 6 | 1 | - | 9 | 2 | 7 | - | 1216.195 | 1201.922 |
| 15.751 | 3 | 2 | 2 | + | 4 | 0 | 4 | + | 222.053 | 206.301 |
| 16.941 | 4 | 3 | 2 | $+$ | 5 | 1 | 4 | + | 399.458 | 382.517 |
| 17.243 | 8 | 4 | 4 | $+$ | 10 | 0 | 10 | + | 1131.776 | 1114.532 |
| 19.244 | 7 | 5 | 2 | $+$ | 9 | 1 | 8 | + | 1079.08 | 1059.836 |
| 24.098 | 5 | 4 | 1 | - | 7 | 0 | 7 | - | 610.341 | 586.244 |
| 24.986 | 4 | 2 | 3 | - | 5 | 0 | 5 | - | 325.348 | 300.362 |
| 25.685 | 6 | 4 | 3 | - | 7 | 2 | 5 | - | 782.41 | 756.725 |
| 26.327 | 8 | 6 | 2 | + | 10 | 2 | 8 | + | 1437.969 | 1411.642 |
| 27.752 | 8 | 5 | 4 | + | 9 | 3 | 6 | + | 1282.919 | 1255.167 |
| 30.488 | 5 | 2 | 4 | + | 6 | 0 | 6 | + | 446.697 | 416.209 |
| 31.169 | 9 | 5 | 4 | + | 10 | 3 | 8 | + | 1477.298 | 1446.128 |
| 33.125 | 9 | 4 | 5 | - | 11 | 0 | 11 | - | 1360.236 | 1327.11 |
| 33.332 | 6 | 2 | 5 | - | 7 | 0 | 7 | - | 586.244 | 552.911 |
| 33.476 | 10 | 2 | 9 | - | 11 | 0 | 11 | - | 1327.11 | 1293.634 |
| 34.099 | 10 | 1 | 9 | - | 11 | 1 | 11 | - | 1327.118 | 1293.018 |
| 34.147 | 9 | 2 | 8 | + | 10 | 0 | 10 | + | 1114.532 | 1080.386 |
| 34.456 | 7 | 2 | 6 | + | 8 | 0 | 8 | + | 744.064 | 709.608 |
| 34.568 | 8 | 2 | 7 | - | 9 | 0 | 9 | - | 920.169 | 885.6 |
| 35.47 | 9 | 1 | 8 | + | 10 | 1 | 10 | + | 1114.55 | 1079.08 |
| 37.107 | 8 | 5 | 3 | - | 10 | 1 | 9 | - | 1293.018 | 1255.912 |
| 37.125 | 1 | 1 | 0 | + | 2 | 1 | 2 | + | 79.496 | 42.372 |
| 37.32 | 8 | 1 | 7 | - | 9 | 1 | 9 | - | 920.21 | 882.89 |
| 37.862 | 5 | 5 | 0 | + | 7 | 1 | 6 | + | 742.076 | 704.214 |
| 38.938 | 5 | 3 | 3 | - | 6 | 1 | 5 | - | 542.906 | 503.968 |
| 39.68 | 8 | 5 | 3 | - | 9 | 3 | 7 | - | 1255.912 | 1216.231 |
| 39.949 | 7 | 1 | 6 | + | 8 | 1 | 8 | + | 744.163 | 704.214 |
| 41.406 | 3 | 3 | 1 | - | 5 | 1 | 5 | - | 326.626 | 285.219 |
| 41.438 | 4 | 4 | 0 | + | 6 | 0 | 6 | + | 488.134 | 446.697 |
| 41.597 | 4 | 4 | 1 | - | 5 | 2 | 3 | - | 488.108 | 446.511 |
| 43.573 | 6 | 1 | 5 | - | 7 | 1 | 7 | - | 586.479 | 542.906 |
| 45.637 | 7 | 4 | 3 | - | 8 | 2 | 7 | - | 931.237 | 885.6 |
| 46.242 | 6 | 5 | 2 | + | 7 | 3 | 4 | + | 888.599 | 842.357 |
| 47.103 | 2 | 1 | 1 | - | 3 | 1 | 3 | - | 142.278 | 95.176 |
| 47.551 | 9 | 5 | 4 | + | 11 | 1 | 10 | + | 1524.848 | 1477.298 |
| 47.795 | 5 | 1 | 4 | + | 6 | 1 | 6 | + | 447.252 | 399.458 |
| 48.172 | 6 | 4 | 2 | $+$ | 7 | 2 | 6 | + | 757.78 | 709.608 |
| 70.138 | 2 | 2 | 0 | + | 3 | 2 | 2 | + | 206.301 | 136.164 |
| 70.757 | 8 | 6 | 2 | + | 9 | 4 | 6 | + | 1411.642 | 1340.885 |
| 71.926 | 4 | 4 | 0 | + | 5 | 2 | 4 | + | 488.134 | 416.209 |
| 71.938 | 6 | 5 | 1 | - | 7 | 3 | 5 | - | 888.633 | 816.694 |
| 72.964 | 8 | 3 | 6 | + | 9 | 1 | 8 | + | 1079.08 | 1006.116 |
| 74.621 | 5 | 5 | 1 | - | 7 | 3 | 5 | - | 816.694 | 742.073 |
| 75.07 | 6 | 3 | 3 | - | 7 | 1 | 7 | - | 661.549 | 586.479 |
| 75.395 | 3 | 0 | 3 | - | 3 | 2 | 1 | - | 212.156 | 136.762 |
| 76.787 | 9 | 3 | 7 | - | 10 | 1 | 9 | - | 1293.018 | 1216.231 |
| 77.255 | 2 | 2 | 1 | - | 3 | 2 | 1 | - | 212.156 | 134.902 |
| 78.72 | 10 | 3 | 8 | + | 11 | 1 | 10 | + | 1524.848 | 1446.128 |
| 79.213 | 8 | 4 | 5 | - | 9 | 2 | 7 | - | 1201.922 | 1122.709 |
| 80.167 | 7 | 7 | 1 | - | 9 | 5 | 5 | - | 1474.981 | 1394.814 |
| 80.524 | 5 | 5 | 1 | - | 6 | 3 | 3 | - | 742.073 | 661.549 |

Table 1 (Cont'd)

| $v, \mathrm{~cm}^{-1}$ | $J^{\prime}$ | $K_{\mathrm{a}}^{\prime}$ | $K_{\mathrm{c}}^{\prime}$ | Parity | $J^{\prime \prime}$ | $K_{\mathrm{a}}^{\prime \prime}$ | $K_{\mathrm{c}}^{\prime \prime}$ | Parity | $E^{\prime}, \mathrm{cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 82.483 | 7 | 7 | 0 | + | 9 | 5 | 4 | + | 1477.298 |
| 82.511 | 5 | 3 | 3 | - | 7 | 1 | 1394.814 |  |  |
| 84.414 | 7 | 6 | 2 | + | 8 | 4 | 7 | $-\mathrm{cm}^{-1}$ |  |
| 85.889 | 2 | 2 | 0 | + | 4 | 0 | 4 | + | 1216.19 |
| 86.717 | 6 | 6 | 0 | + | 8 | 4 | 4 | 1131.776 |  |
| 87.168 | 10 | 2 | 8 | + | 11 | 2 | 10 | + | 222.053 |
| 88.206 | 3 | 2 | 1 | - | 4 | 2 | 3 | 136.164 |  |
| 91.317 | 10 | 4 | 6 | + | 11 | 2 | 10 | + | 151.776 |
| 1045.059 |  |  |  |  |  |  |  |  |  |

Note: $v$ is the rotational transition wavenumber; $J$ is the quantum number of the total angular (rotational) momentum; $K_{\mathrm{a}}$ is the quantum number of the projection of the total momentum $J$ for the corresponding level in the limiting case of a prolate symmetric top; $K_{\mathrm{c}}$ is the momentum projection value in the limiting case of an oblate symmetric top; $E$ is the molecular energy level, with the superscripts' and " indicating the upper and lower transition levels, respectively, and parity of levels denoted by positive $(+)$ and negative $(-)$ signs.
(iii) The remark by Krupnov and Tretyakov [2] concerning the illegitimacy of the term 'libration' in the title of the paper by Bunkin et al. [1] is correct. In the discussion of this term, the authors of Ref. [2] clearly formulated why narrow lines that arise from molecular rotational transitions cannot occur in the liquid phase.

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