## LETTERS TO THE EDITORS

## On the observation of molecular rotational spectra in condensed media

M A Bol'shov, A A Makarov, V P Mironenko

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<u>Abstract.</u> This letter was written in connection with the paper by A F Bunkin, A A Nurmatov, and S M Pershin (*Usp. Fiz. Nauk* 176 883 (2006) [*Phys. Usp.* 49 855 (2006)]) and the comments on this paper by A F Krupnov and M Yu Tretyakov (*Usp. Fiz. Nauk* 179 1363 (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 H<sub>2</sub>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  $cm^{-1}$  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-cm<sup>-1</sup> line

M A Bol'shov, A A Makarov, V P Mironenko Institute of Spectroscopy, Russian Academy of Sciences, ul. Fizicheskaya 5, 142190 Troitsk, Moscow region, Russian Federation Tel. (7-496) 751 02 27 E-mail: bolshov@isan.troitsk.ru

Received 3 April 2009 Uspekhi Fizicheskikh Nauk **179** (12) 1368–1370 (2009) DOI: 10.3367/UFNr.0179.200912q.1368 Translated by E N Ragozin; edited by A Radzig 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 a cm<sup>-1</sup>, is perplexing. As is well known, even in liquid <sup>3</sup>He, which exhibits the weakest interaction with impurity molecules, the rotational spectrum does not manifest itself, and the linewidths of vibrational transitions are  $\ge 1 \text{ cm}^{-1}$  [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 vibrational– rotational 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 CCl<sub>4</sub> and OH molecular spectra. For reasons unknown to us, Bunkin et al. [1] indicated the CCl<sub>4</sub> line positions by nonequidistant dotted lines, while the vibrational–rotational lines of the CCl<sub>4</sub> molecule ( $T_d$  symmetry) are equidistant.

Table 1.

<i>v</i> , cm <sup>-1</sup>	J'	$K'_{\rm a}$	$K_{\rm c}'$	Parity	J''	$K_{\rm a}^{\prime\prime}$	<i>K</i> <sub>c</sub> "	Parity	$E', \mathrm{cm}^{-1}$	$E'', \operatorname{cm}^{-1}$
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	I	5	—	/	1	7	_	586.479	542.906
45.637	7	4	3	_	8	2	/	_	931.237	885.0
46.242	6	5	2	+	./	3	4	+	888.599	842.557
47.103	2	I	I	_	3	1	3	_	142.278	95.170
47.551	9	5	4	+		1	10	+	1524.848	200.459
47.795	5	I	4	+	6	1	6	+	447.252	399.438 700.608
48.172	6	4	2	+	2	2	0	+	/5/./8 206.201	126 164
70.138	2	2	0	+	3	2	2	+	200.301	1240 885
70.757	8	6	2	+	9	4	0	+	1411.042	1540.885
71.926	4	4	0	+	5	2	4	+	466.134	410.209 816 604
71.938	6	5	I	_	/	5	5	_	888.033 1070.08	1006 116
72.964	8	3	6	+	9	1	8	+	10/9.08 816.604	742.072
74.621	5	5		_	7	1	с 7	_	661 540	586 470
/5.0/	6	3	5	_	2	2	1	_	212 156	136 762
/5.395	3	0	5	_	3	2	1	_	1202.019	1216 221
76.787	9	3	1	_	10	2	9	_	212 156	1210.231
79.72	2	2	0	_	3	1	10	_	1524 949	134.902
/8./2	10	5	8	+	11	2	10	+	1201 022	1122 700
79.213	8	4	5	_	9	5	5	_	1201.922	1304 814
80.167	/	/	1	_	9	2	2	_	7/2 072	661 540
80.524	5	3	1	_	0	3	3	_	142.075	001.349

## Table 1 (Cont'd)

v, cm <sup>-1</sup>	J'	$K'_{ m a}$	$K_{ m c}'$	Parity	J''	$K_{\rm a}^{\prime\prime}$	$K_{\rm c}^{\prime\prime}$	Parity	$E', \mathrm{cm}^{-1}$	$E'',  {\rm cm}^{-1}$
82.483	7	7	0	+	9	5	4	+	1477.298	1394.814
82.511	5	3	3	_	7	1	7	_	586.479	503.968
84.414	7	6	2	+	8	4	4	+	1216.19	1131.776
85.889	2	2	0	+	4	0	4	+	222.053	136.164
86.717	6	6	0	+	8	4	4	+	1131.776	1045.059
87.168	10	2	8	+	11	2	10	+	1525.136	1437.969
88.206	3	2	1	_	4	2	3	-	300.362	212.156
91.317	10	4	6	+	11	2	10	+	1616.453	1525.136

*Note:* v is the rotational transition wavenumber; J is the quantum number of the total angular (rotational) momentum;  $K_a$  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;  $K_c$  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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