ISSN 0030-400X, Optics and Spectroscopy, 2022, Vol. 130, No. 2, pp. 62–67. © Pleiades Publishing, Ltd., 2022.
Russian Text © The Author(s), 2021, published in Optika i Spektroskopiya, 2021, Vol. 129, No. 10, pp. 1244–1248.

Parameters of the Water Vapor Line Contour at Helium Broadening

N. N. Lavrent'eva[a], * and A. S. Dudarenok[a], **

[a] *V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Science (IAO SB RAS), Tomsk, 634021 Russia*

**e-mail: lnn@iao.ru*

***e-mail: dudaryon@iao.ru*

Received May 25, 2021; revised May 25, 2021; accepted July 9, 2021

Abstract—The method of medium frequencies has been applied to calculate the collisional half-widths of vibrational-rotational lines of a water molecule under helium pressure. The calculations have been performed for a wide range of rotational quantum numbers (J from 0 to 20: the calculations have been made by the method of medium frequencies, and J from 20 to 50: the interpolation of dependence on J has been performed). The spectral range has been from 500 to 10000 cm^{-1}. The H_2O–He line broadening coefficients obtained by us have been compared with the literature data and a good agreement has been obtained. The coefficients of the temperature dependence of the lines half-widths have been calculated.

Keywords: line broadening, intermolecular interaction, averaged energy difference method, temperature exponent

DOI: 10.1134/S0030400X22010088

The data presented in the article are necessary, first, for astrophysical applications, in particular, when modeling the spectra of low-temperature stars, where it is necessary to know the shock parameters of the H_2O lines contour by the helium and hydrogen pressures in a wide temperature range. Hydrogen and helium are the most common substances in the universe. They make up most of the atmospheres of cold stars, giant planets, and exoplanets (planets outside the Solar system). The broadening of the water vapor vibrational-rotational lines by the pressure of hydrogen and helium at high temperatures has been poorly studied. In this paper, the broadening of the water molecule vibrational-rotational lines by helium pressure at high temperatures up to 2000 K.

The data available in the literature are clearly insufficient: single measurements of the H_2O–He broadening coefficients are presented in [1–16] and the most extensive experimental values are given in [17–23]. The calculated data are presented in [23] together with the measured coefficients of the broadening of water vapor lines by helium pressure for an extensive list of lines on 11 absorption bands. The coefficients of temperature dependence in the literature are obtained only for the case of broadening of two lines ($3_{13} \leftarrow 2_{20}$ and $4_{14} \leftarrow 3_{21}$) at temperatures of 80–600 K [1–3] by helium pressure, as well as by hydrogen pressure. In [12], the low-temperature measurements were carried out for the $1_{10} \leftarrow 1_{01}$ line in the range of 17–200 K. A very weak temperature dependence was found for this line.

To calculate the lines contour shock parameters, several methods are currently used, among which are various modifications of the Robert–Bonami method [24], the modified Robert–Bonami complex formalism [25], and the semi-empirical method [26]. Recently, a method of medium frequencies has been proposed [27], which makes it possible to quickly calculate the coefficients of broadening of vibrational-rotational lines of the asymmetric top molecules on the basis of a small amount of empirical data. The idea of the method is that a part of the values that reflect the influence of the buffer molecule on the internal state of the absorbing molecule is isolated from the entire calculation scheme. These values strongly depend on the absorbing molecule quantum indices. Of these, the value that is called the medium frequency of collision transitions is compiled. By virtual transitions, we mean all possible transitions from a certain energy level caused by collisions. The medium frequency of virtual transitions for the line $i \rightarrow f$ is determined by the following expression:

$$\bar{\omega}_{if} = \frac{1}{W}\left\{\sum_{i'}(2i'+1)D^2\left(ii'|l\right)f(\omega_{ii'})\omega_{ii'} + \sum_{f'}(2f'+1)D^2\left(ff'|l\right)f(\omega_{ff'})\omega_{ff'}\right\}, \quad (1)$$

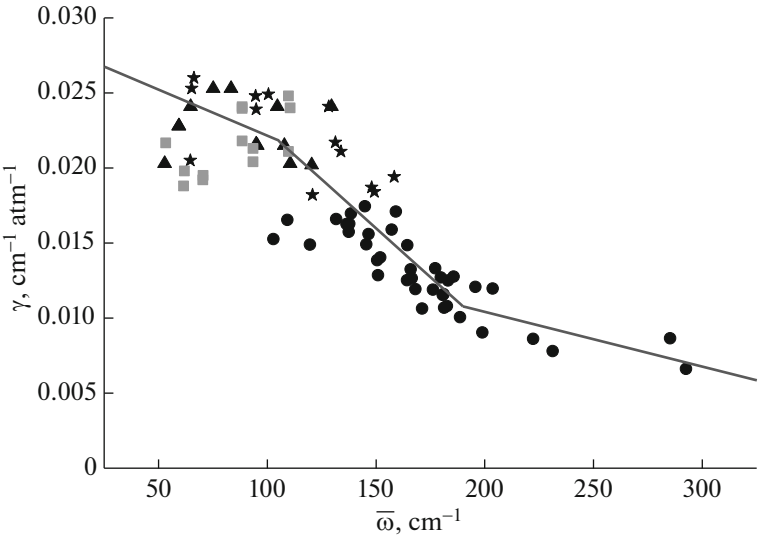

Fig. 1. Experimental half-widths of the H_2O–He lines depending on the medium frequency of the collision transitions. The squares represent data in [3–6, 9, 10, 12], triangles—in [20], circles—in [21], stars—in [22], line—approximation.

where $W = \sum_{i'}(2i'+1)D^2(ii'|l)f(\omega_{ii'}) + \sum_{f'}(2f'+1)D^2(ff'|l)f(\omega_{ff'})$.

Here, $\omega_{ii'}$ and $\omega_{ff'}$ are the collision (virtual) transitions frequencies, $D^2(ii'|l)$ and $D^2(ff'|l)$ are the matrix elements of the dipole ($l = 1$) and quadrupole ($l = 2$) moments of virtual transitions, and $f(\omega_{ii'})$ and $f(\omega_{ff'})$ are resonance functions. It can be seen that the averaging takes place over all virtual transitions, as well as over the lower and upper energy states forming this transition $i \to f$.

Knowing the correspondence between the values $\bar{\omega}_{if}$ (calculated in advance for all possible transitions up to $J = 20$) and the lines quantum identification, we compare the collision coefficients of the broadening of the lines with the $\bar{\omega}_{if}$ values. According to the latter dependence, we obtain an approximation in the form of some simple expression. Usually this is a rectilinear or quadratic dependence, according to which it is possible to restore the lines half-widths.

When applying the medium frequencies method, first, it is necessary to identify the most verified literary data. Since the experimental half-widths of water vapor lines induced by helium pressure in [20–22] are in good agreement with each other, we used them to implement the medium frequencies method. Figure 1 shows the dependence of the broadening coefficients on the medium frequency of collision transitions for the case of H_2O–He, as well as the corresponding approximation depending on the medium frequency of collision transitions. Here, the most extensive measurements in [20–22] are shown in black symbols and all single data in [3–6, 9, 10, 12]—by gray squares.

The following approximation by three straight line segments is obtained:

$$\gamma_{if} = -0.0000615\bar{\omega}_{if} + 0.02830 \quad \text{at} \quad 0 < \bar{\omega}_{if} \le 105,$$
$$\gamma_{if} = -0.0001302\bar{\omega}_{if} + 0.03552 \quad \text{at} \quad 105 < \bar{\omega}_{if} \le 190, \qquad (2)$$
$$\gamma_{if} = -0.0000364\bar{\omega}_{if} + 0.01769 \quad \text{at} \quad \bar{\omega}_{if} > 190.$$

Then the line broadening coefficients were calculated using Eq. (2) for the values of the rotational quantum number $J \le 20$. A part of the data obtained in this way is presented in [28]. There are no experimental data for larger values of $20 < J \le 50$, therefore, an approximation of the values γ on J was used to obtain them. For this purpose, the most verified data for the lower vibration bands were collected [3–5, 9, 10, 12, 20–22] and the H_2O–He broadening coefficients were plotted depending on the rotational quantum number J and then averaged over the quantum numbers K_a and K_c. The measured coefficients of broadening of the lines of the rotational band, the ν_2 band, and $2\nu_1$ band depending on J are shown in Fig. 2. Also, the averaged values of the lines half-widths for all quantum numbers K_a and the approximation are plotted in the figure.

The rotational dependence of the lines half-widths for the case of helium broadening in comparison with the case of hydrogen broadening [29] constructed according to the literature data is shown in Fig. 3. It can be seen that the half-widths of the H_2O–H_2 lines are, on average, 2.5 times larger than the half-widths of the H_2O–He lines, which is due to the large quad-

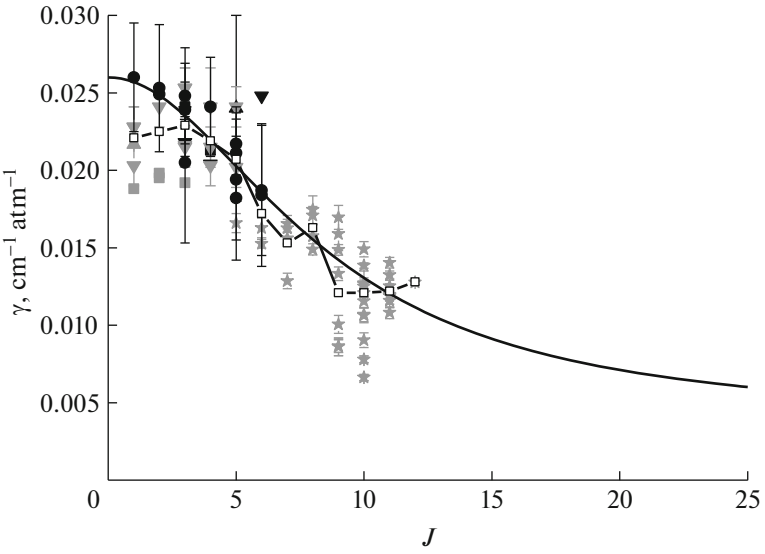

Fig. 2. Rotational dependence of the half-widths of the lines for the case of H_2O–He. Black squares, triangles, inverted triangles, stars indicate data in [3], [4], [5], [9], respectively; gray squares, triangles, inverted triangles, stars indicate data in [10], [12], [20], [21], respectively; the black circles indicates data in [22], the line with hollow squares indicates the average values for a certain rotational quantum number *J*, and the line indicates an approximation.

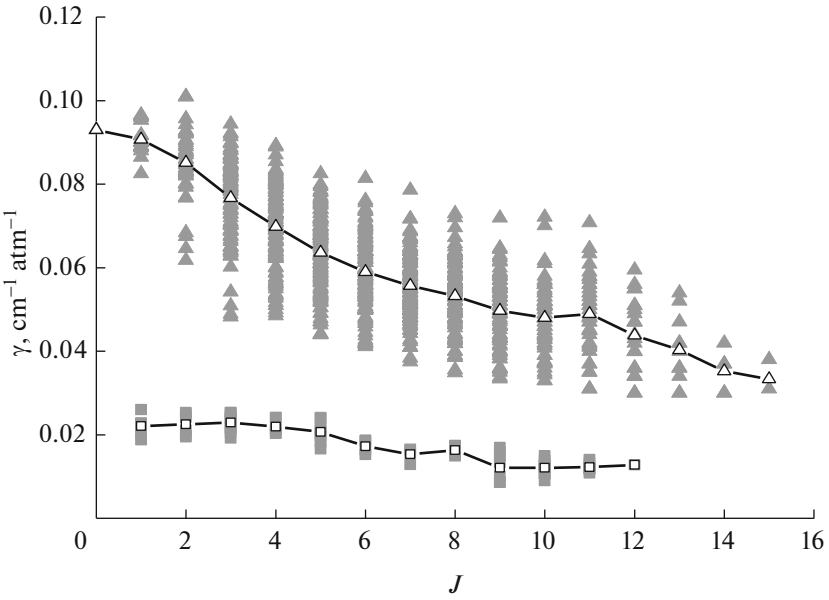

Fig. 3. The broadening coefficients of the water vapor lines by hydrogen and helium pressure depending on the rotational quantum number *J*. Gray triangles and squares denote sets of measured values and a line with hollow triangles and squares—the average values for a certain rotational quantum number *J* for the H_2O–H_2 and H_2O–He mixtures, respectively.

rupole moment of the H_2 molecule compared to that of the He atom.

The lines half-widths for the H_2O–H_2 system both in the purely rotational band and in other vibrational absorption bands are calculated using the medium frequencies obtained for the rotational band and are in good agreement with experimental data because of the weak vibrational dependence of the lines half-widths. However, as shown in [23], the measured lines half-widths for the H_2O–He gas mixtures cannot change by more than 10% when switching from one absorption band to another. Therefore, for such a buffer gas as helium, the medium frequencies for excited states were changed to obtain more accurate the lines half-

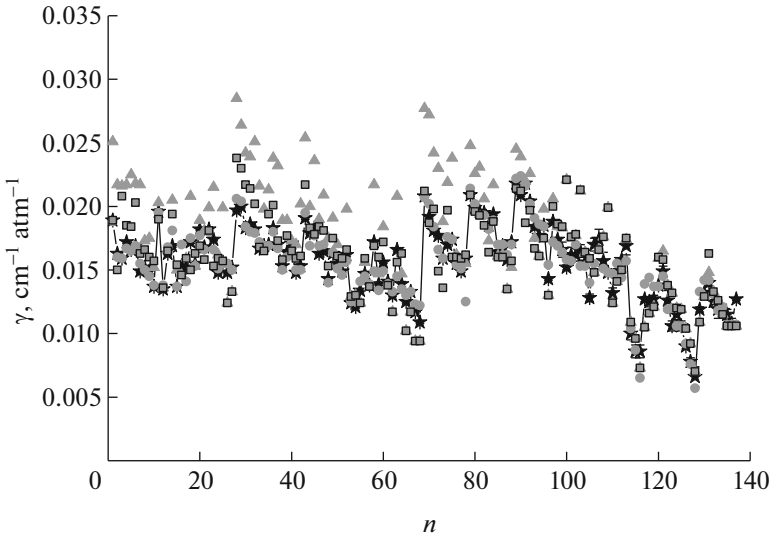

Fig. 4. The broadening coefficients of the H_2O lines by He pressure calculated by the medium frequency method without considering Eq. (4) (triangle) and using Eq. (4) (square), in comparison with (line with stars) experimental and (circles) theoretical data [23]. The line number n corresponds to an increase in the transition frequency.

widths. Figure 4 shows a comparison of the half-widths of the lines calculated by us without considering the oscillatory dependence with the experimental and calculated data obtained in [1]. The maximum mismatch in the data is observed for small frequencies of collision transitions.

In [27], to clarify the vibrational dependence of the half-widths of the lines for the H_2O–N_2 system, a formula for calculating the medium frequencies of the collision transitions in the vibrational band $\bar{\omega}(\nu_1\nu_2\nu_3)$ as the sum of the medium frequency for the rotational band and the medium frequency differences for the first excited state ν_1, ν_2, and ν_3 multiplied by the number of vibrational quanta corresponding to a certain vibration was proposed:

$$\bar{\omega}(\nu_1\nu_2\nu_3) = \bar{\omega}(000) + \nu_1[\bar{\omega}(100) - \bar{\omega}(000)] + \nu_2[\bar{\omega}(010) - \bar{\omega}(000)] + \nu_3[\bar{\omega}(001) - \bar{\omega}(000)]. \quad (3)$$

The equation adequately describes the behavior of line broadening with a weak dependence on vibrational quantum numbers (e.g., in the case of H_2O–N_2). However, in the case of broadening with atomic helium, when a strong vibrational dependence of the half-widths is manifested, its use is unacceptable. Therefore, this equation was modified by introducing multipliers before the differences that were obtained from experimental the half-widths of the lines in the bands: $2\nu_1$, $2\nu_2$, and $2\nu_2 + \nu_3$ [23] (one transition was used in each band):

$$\bar{\omega}(\nu_1\nu_2\nu_3) = \bar{\omega}(000) + a_1\nu_1[\bar{\omega}(100) - \bar{\omega}(000)] + a_2\nu_2[\bar{\omega}(010) - \bar{\omega}(000)] + a_3\nu_3[\bar{\omega}(001) - \bar{\omega}(000)],$$

where

$$a_1 = 0.14954\bar{\omega} - 22.431,$$
$$a_2 = -0.06477\bar{\omega} + 9.715, \quad (4)$$
$$a_3 = 0.08684\bar{\omega} - 14.527.$$

Figure 5 shows the dependence of the experimental the lines half-width [3–6, 9, 10, 12, 20–23] on the

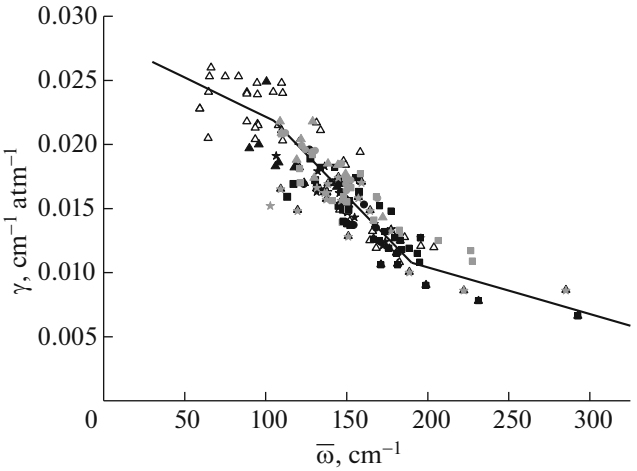

Fig. 5. The broadening coefficients of the H_2O lines by He pressure depending on the frequencies of collision transitions. Black squares, circles, triangles, stars denote the measured values in [23] in the bands $2\nu_2$, ν_1, $\nu_1 + \nu_2$, and $\nu_2 + \nu_3$, respectively; gray squares, circles, triangles, stars denote the measured values in [23] in the bands $2\nu_2 + \nu_3$, $2\nu_1$, $\nu_1 + \nu_3$, and in the rotational band, respectively; hollow triangles—in [3–6, 9, 10, 12, 20–22]; and the line is an approximation for the medium frequency method.

medium frequency of collision transitions obtained by Eq. (4). The measured values in [23] are sketched separately for each vibrational band. After recalculating the parameters $\bar{\omega}$ according to Eq. (4), the approximation coefficients in Eq. (2) obtained for low vibrational bands will be the same. The standard deviations of the calculated half-widths of the lines without using the modification in Eq. (4) and using modification in Eq. (4) from the experimental data in [23] will be 0.0029 cm^{-1} atm^{-1} and 0.0017 cm^{-1} atm^{-1}, respectively.

For the applications in astrophysics, in particular, when modeling the spectra of low-temperature stars, it is necessary to know the lines contour shock parameters in a wide temperature range. The temperature dependence coefficients N for the broadening of two water vapor lines ($3_{1\,3} \leftarrow 2_{2\,0}$ and $4_{1\,4} \leftarrow 3_{2\,1}$) by helium pressure determined in the temperature range of 80–600 K are given in [1–3]. In this paper, the temperature index for the case of H_2O–He was defined as the ratio to the values of N for the case of H_2O–H_2:

$$N^{H_2O-He} = 0.576N^{H_2O-H_2}, \quad (5)$$

where $N^{H_2O-H_2}$ is obtained by the medium frequency method in [29]. The multiplier in Eq. (5) was obtained from the measured data [3].

The calculations of the line broadening coefficients and their temperature parameters for the H_2O–He mixture are carried out in the work. The quantum number of the total angular momentum varies in the range from 0 to 50. It is shown that when studying the broadening of water vapor lines by helium pressure in a wide spectral range, it is necessary to consider the dependence on vibrational excitation. The approximation expression for the vibrational dependence that allows us to adequately describe the available experimental data is obtained. Thus, the medium frequency method developed by the authors on the basis of the assessment of the contributions of collision transitions to the half-width of the spectral line makes it possible to calculate the half-width of the lines of the asymmetric top molecules with an accuracy close to the one of modern computational and experimental methods, without resorting to a complex computational scheme. The half-widths of the lines of the H_2O–He molecules calculated using the proposed method are in good agreement with various experimental and calculated data.

FUNDING

The work was carried out within the framework of the state assignment of the IAO SB RAS and RFBR grant no. 19-03-00389.

CONFLICT OF INTEREST

The authors state that they have no conflicts of interest.

REFERENCES

1. M. Godon and A. Bauer, Chem. Phys. Lett. **147**, 189 (1988). https://doi.org/10.1016/0009-2614(88)85081-4
2. T. M. Goyette and F. C. Lucia, J. Mol. Spectrosc. **143**, 346 (1990). https://doi.org/10.1016/0022-2852(91)90099-V
3. J. M. Dutta, C. R. Jones, T. M. Goyette, and F. C. Lucia, Icarus **102**, 232 (1993). https://doi.org/10.1006/icar.1993.1046
4. V. V. Lazarev, Y. N. Ponomarev, B. Sumpf, O. Fleischmann, J. Waschull, H. D. Kronfeldt, and V. N. Stroinova, J. Mol. Spectrosc. **173**, 177 (1995). https://doi.org/10.1006/jmsp.1995.1227
5. R. R. Gamache, R. Lynch, and L. R. Brown, J. Quant. Spectrosc. Radiat. Transf. **56**, 471 (1996). https://doi.org/10.1016/0022-4073(96)00098-2
6. M. Lepere, A. Henry, A. Valentin, and C. Camy-Peyret, J. Mol. Spectrosc. **208**, 25 (2001). https://doi.org/10.1006/jmsp.2001.8372
7. V. Zeninary, B. Parvitte, D. Courtois, I. Pouchetm, G. Durry, and Yu. N. Ponomarev, Atmos. Ocean. Opt. **16**, 189 (2003).
8. V. Zeninary, B. Parvitte, D. Courtois, N. N. Lavrentieva, Yu. N. Ponomarev, and G. Durry, Mol. Phys. **102**, 1697 (2004). https://doi.org/10.1080/00268970412331287133
9. G. Yu. Golubiatnikov, J. Mol. Spectrosc. **230**, 196 (2005). https://doi.org/10.1016/j.jms.2004.10.011
10. L. R. Brown, D. C. Benner, V. M. Devi, M. A. H. Smith, and R. A. Toth, J. Mol. Struct. **742**, 111 (2005). https://doi.org/10.1016/j.molstruc.2004.12.059
11. D. Lisak, J. T. Hodges, and R. Ciuryło, Phys. Rev. A **73**, 012507 (2006).
12. M. J. Dick, B. J. Drouin, and J. C. Pearson, J. Quant. Spectrosc. Radiat. Transf. **110**, 619 (2009). https://doi.org/10.1016/j.jqsrt.2008.11.012
13. A. M. Solodov and V. I. Starikov, Mol. Phys. **107**, 43 (2009). https://doi.org/10.1080/00268970802698655
14. K. Yu. Osipov, V. A. Kapitanov, A. E. Protasevich, A. A. Pereslavtseva, and Ya. Ya. Ponurovsky, J. Quant. Spectrosc. Radiat. Transf. **142**, 1 (2014). https://doi.org/10.1016/j.jqsrt.2014.03.003
15. V. I. Starikov, Opt. Spectrosc. **116**, 238 (2014).
16. C. Claveau, A. Henry, D. Hurtmans, and A. Valentin, J. Quant. Spectrosc. Radiat. Transf. **68**, 273 (2001). https://doi.org/10.1016/S0022-4073(00)00025-X
17. A. E. Protasevich and V. I. Starikov, Opt. Spectrosc. **98**, 577 (2005).
18. A. M. Solodov and V. I. Starikov, Opt. Spectrosc. **108**, 19 (2008).
19. C. Claveau and A. Valentin, Mol. Phys. **107**, 1417 (2009). https://doi.org/10.1080/00268970902911404
20. A. Lucchesinia, S. Gozzini, and C. Gabbanini, Eur. Phys. J. D **8**, 223 (2000).

21. D. W. Steyert, W. F. Wang, J. M. Sirota, N. M. Donahue, and D. C. Reuter, J. Quant. Spectrosc. Radiat. Transf. **83**, 183 (2004). https://doi.org/10.1016/S0022-4073(02)00300-X

22. P. Poddar, S. Mitra, M. M. Hossain, D. Biswas, P. N. Ghosh, and B. Ray, Mol. Phys. **108**, 1957 (2010). https://doi.org/10.1080/00268976.2010.499376

23. T. M. Petrova, A. M. Solodov, A. A. Solodov, and V. I. Starikov, J. Quant. Spectrosc. Radiat. Transf. **129**, 241 (2013). https://doi.org/10.1016/j.jqsrt.2013.06.021

24. D. Robert and J. Bonamy, J. Phys. (Fr.) **40**, 923 (1979). https://doi.org/10.1051/jphys:019790040010092300

25. Q. Ma, R. H. Tipping, and C. Boulet, J. Quant. Spectrosc Radiat Transf. **103**, 588 (2007). https://doi.org/10.1016/j.jqsrt.2006.08.001

26. A. Bykov, N. Lavrentieva, and L. Sinitsa, Mol. Phys. **102**, 1653 (2004). https://doi.org/10.1080/00268970410001725765

27. A. S. Dudaryonok, N. N. Lavrentieva, and Q. Ma, Atmos. Ocean. Opt. **28**, 503 (2015). https://doi.org/10.1134/S1024856015060056

28. E. J. Barton, C. Hill, S. N. Yurchenko, J. Tennyson, A. S. Dudaryonok, and N. N. Lavrentieva, J. Quant. Spectrosc. Radiat. Transf. **187**, 453 (2017). https://doi.org/10.1016/j.jqsrt.2016.10.024

29. N. N. Lavrent'eva and A. S. Dudarenok, Opt. Atmosf. Okeana **29**, 828 (2016).

Translated by N. Petrov