

# Calculation of the self-broadening coefficients of D<sub>2</sub>O absorption lines using the exact trajectory model

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The self-broadening coefficients  $\gamma$  and pressure-induced frequency shift coefficients  $\delta$  of the  $\nu_2$ ,  $\nu_1 + \nu_2$ ,  $3\nu_2$ , and  $\nu_2 + \nu_3$  vibrational-rotational bands of D<sub>2</sub>O molecule were calculated in the framework of the semiclassical approach, taking into account the exact trajectory model. The influence of the accidental resonances on values of  $\gamma$  and  $\delta$  was investigated. The computed coefficients  $\gamma$  were fitted to an empirical expression.

## Introduction

Water vapor is a subject of numerous spectroscopic investigations. The main attention is paid to its isotopic modification H<sub>2</sub><sup>16</sup>O, while other modifications are meant to be less significant. Nevertheless, the study of spectroscopic properties of H<sub>2</sub>O isotopic modifications gives an additional information about its parameters. Therefore, the study of vibrational-rotational (VR) spectra of H<sub>2</sub>O isotopes is of constant interest.

This paper presents the calculation of self-broadening coefficient  $\gamma$  and self-shift (i.e., by its own pressure) coefficient  $\delta$  for  $\nu_2$  band, which is well studied for high values of rotational quantum numbers  $J \sim 25$ ,  $K_a \sim 25$ . This gives a possibility to investigate asymptotic behavior of these coefficients.

Besides, the influence of accidental resonances on  $\gamma$  and  $\delta$  in the water vapor molecule was also studied. For a given purpose, the D<sub>2</sub><sup>16</sup>O molecule is even more suitable object of investigation than H<sub>2</sub><sup>16</sup>O, because the accidental resonances in it for lower polyads of interacting states manifest themselves even at low values of the rotational quantum number  $J$ . Finally, we determined parameters of analytical model for self-broadening coefficients  $\gamma$ , allowing the calculation of these coefficients and their temperature dependence without semiclassical calculation methods. These calculations may be useful for estimation of  $\gamma$  of different vibrational bands of D<sub>2</sub><sup>16</sup>O.

## Calculation method

For vibrational-rotational absorption line  $(i) \rightarrow (f)$  ( $i$  and  $f$  are a totality of VR quantum numbers)  $\gamma_{if}$   $\delta_{if}$  coefficients were determined by the following formula:

$$\gamma_{if} + i\delta_{if} = \frac{n}{c} \sum_{J_2} \rho_{J_2} \sigma_{J_2}, \quad (1)$$

in which the complex parameter  $\sigma_{J_2}$  was calculated by the Robert–Bonami method<sup>1</sup> with the use of the following relation

$$\sigma_{J_2} = \int_0^\infty v F(v) dv \int_{r_0}^\infty D r_c dr_c \left[ 1 - (1 - S_2^{\text{middle}'}) \times \exp(-iS_1 - S_{2,i}^{\text{outer}} - S_{2,f}^{\text{outer}*} - S_2^{\text{middle}'}) \right], \quad (2)$$

where  $D$  is the Jacobian of transition from variables  $\{b, v\}$  to  $\{r_c, v\}$  ( $b$  is the target parameter,  $r_c$  is the shortest distance between interacting molecules), quantity  $r_0$  was determined in Ref. 1;  $S_2^{\text{middle}'}$  denotes the part of  $S_2^{\text{middle}}$  which is diagonal over quantum numbers of the disturbing molecule and  $S_2^{\text{middle}'} = S_{2,i}^{\text{middle}} - S_{2,i}^{\text{middle}'}$ . Besides,  $n$  in Eqs. (1) and (2) is the gas density;  $J_2$  are quantum numbers for rotational state of the disturbing molecule;  $\rho_{J_2}$  is the statistical weight of this state;  $F(v)$  is the Boltzmann function of molecules distribution over speeds  $v$ . All formulas for interruption functions  $S(b)$  are taken from Ref. 2, but the model resonant functions (MET-functions) were used in them, i.e., they are the model representations for functions obtained in the model of exact trajectories. These functions were defined in Refs. 3–6 for the isotope potential, chosen in the form of the Lennard-Johnes potential. Their application to calculation of self-broadening coefficients of absorption lines for a series of vibrational bands of the basic isotopic modification allowed a substantial improving of the calculation quality.<sup>6</sup> In this paper, like in Ref. 6, parameters  $\epsilon/k_B = 356$  K,  $\sigma = 2.725$  Å were used for the Lennard-Johnes potential. Note that several sets of parameters of this potential for water vapor are given in some works. For example, values of 11 such sets are discussed in Ref. 7.

Parameters  $\epsilon$  and  $\sigma$  used in this work were obtained from the second virial coefficient.<sup>8</sup> Just they improve the quality of retrieval of  $\gamma$  and  $\delta$  coefficients for the basic isotopic modification.<sup>6</sup> The values of electrooptic parameters for D<sub>2</sub><sup>16</sup>O molecule were the same as for H<sub>2</sub><sup>16</sup>O (see Ref. 3).

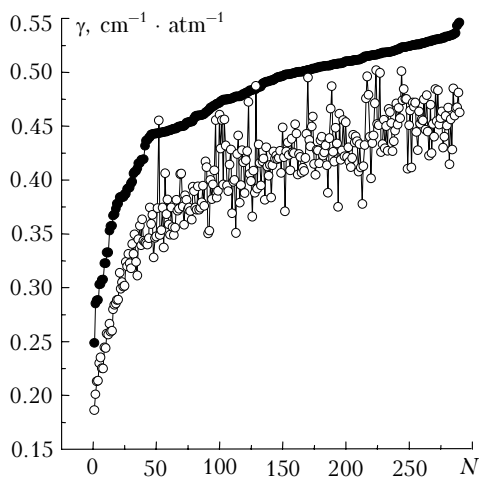
## Band $\nu_2$

This band has been studied<sup>9</sup> up to large quantum numbers  $J \sim 25$ ,  $K_a \sim 25$ . The data from Ref. 9 on

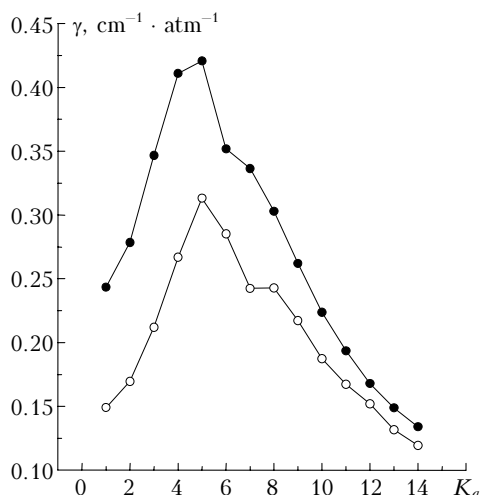
rotational energy levels of the ground and (010) vibrational states were used for obtaining wave functions, necessary for calculations of broadening and shift coefficients. The method of VR-wave function obtaining was described in Refs. 3 and 10.

Coefficients  $\gamma$  and  $\delta$  were calculated for transitions with rotational quantum numbers of final state  $J_f = 25$ ,  $K_{a,f} = 25$  for  $\Delta J = J_f - J_i = 0, \pm 1$ ,  $\Delta K = |K_{a,f} - K_{a,i}| = 1, 3$  at the room temperature  $T = 296$  K. For temperatures 216, 256, 400, 600, 800, and 1200 K the calculations were performed for  $J_f = 15$ ,  $K_{a,f} = 15$  with  $\Delta J = 0, \pm 1$ ,  $\Delta K = 1; 3$ . About 20 820 values of  $\gamma$  and the same quantity for  $\delta$  were calculated.

The comparison of  $\gamma$  coefficients calculated for  $D_2^{16}O$  and  $H_2^{16}O$  lines, which have the same set of rotational quantum numbers of lower and upper states is shown in Figs. 1 and 2. In Fig. 2 the data are arranged in the order of  $\gamma$  increase for  $D_2^{16}O$  lines.



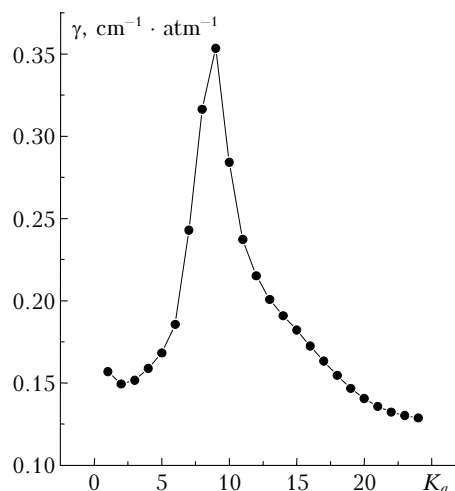
**Fig. 1.** The comparison of self-broadening coefficients  $\gamma$  for lines of  $v_2$  band ( $J_f < 7$ ) in molecules  $H_2^{16}O$  (white dots) and  $D_2^{16}O$  (black dots).



**Fig. 2.** The dependence of self-broadening coefficients  $\gamma$  for  $[J, K_a, K_c] \rightarrow [J, K_a + 1, K'_c]$  lines of  $v_2$  band ( $J = 15$ ) in molecules  $H_2^{16}O$  (white dots) and  $D_2^{16}O$  (black dots).

The dependence on rotational quantum number  $K_a$  is shown in Fig. 2. It is seen that calculated

values of  $\gamma$  for  $D_2^{16}O$  are systematically higher than for  $H_2^{16}O$ . However, the ratio  $\gamma_{D_2O}/\gamma_{H_2O}$  changes from line to line and in the asymptotic behavior of high values of rotational quantum numbers  $J$  or  $K_a$  it is close to unit. The calculated asymptotic behavior of the self-broadening coefficient is shown in Fig. 3.



**Fig. 3.** The asymptotic dependence of the self-broadening coefficient  $\gamma$  on the quantum number  $K_a$  ( $J = 25$ ) for lines  $[J, K_a, K_c] \rightarrow [J - 1, K_a + 1, K'_c]$  of  $v_2$  band of  $D_2^{16}O$  molecule.

It is seen that at a given rotational quantum number  $J = 25$  in the band with  $\Delta J = -1$  the dependence on  $K_a$  has its maximum at  $K_a \sim 10$  and for  $K_a \rightarrow J$  values of  $\gamma$  tends to a constant. This standard behavior is also observed for other transitions.

### Bands $v_1 + v_2$ , $3v_2$ , and $v_2 + v_3$

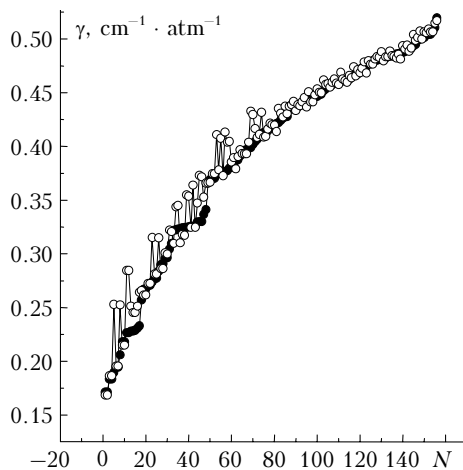
To obtain wave functions of interacting vibrational states (110), (030), and (011) from the second triad, data from Ref. 11 were used. Calculation of wave functions was performed for  $J \leq 10$ . The resonant interactions in this triad occur even at low values of rotational quantum number  $J$ . Mixing coefficients for wave functions of rotational energy levels from  $J = 8$  vibrational state (110) are presented in Table 1. They indicate that these energy levels, possibly, except for the last pair, are in a strong resonance interaction with the energy levels of other vibrational states (030) and (011).

To study the influence of accidental resonances on the values of  $\gamma$  and  $\delta$ , we additionally have obtained wave functions in the model of isolated vibrational states (110), (030), and (011). The values of  $\gamma$  and  $\delta$ , calculated for  $v_1 + v_2$  band in two approximations are exemplified in Figs. 4 and 5.

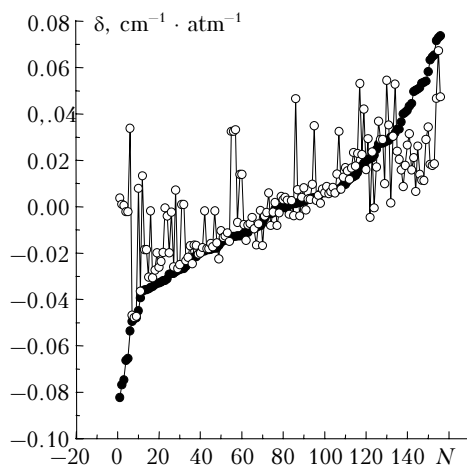
In the first approximation the state (110) was considered along with vibrational states (030) and (011) (resonance approximation), while in the second one this state was considered as an isolated one (approximation of an isolated state). Maximal difference (about 25%) in  $\gamma$  values was achieved at the transitions, for which the mixing coefficient of energy levels, involved in transitions from Table 1, is about 50%.

**Table 1. Mixing coefficient (%) of wave functions for energy levels with  $J = 8$  of (110) vibrational state of  $D_2^{16}O$  molecule**

Calculated energy levels, $cm^{-1}$	$JK_aK_c$	(030)	(110)	(011)
4223.4252	8 0 8	14.47	71.29	14.24
4223.5954	8 1 8	14.40	71.27	14.32
4297.4951	8 1 7	19.35	71.97	8.67
4301.3137	8 2 7	18.38	72.05	9.58
4347.0851	8 2 6	23.82	69.88	6.30
4370.2034	8 3 6	21.04	72.46	6.49
4385.4684	8 3 5	24.23	70.79	4.98
4443.0456	8 4 5	21.01	72.95	6.04
4444.6860	8 4 4	21.32	71.65	7.04
4530.0547	8 5 4	17.51	71.40	11.09
4529.9749	8 5 3	17.25	70.35	12.40
4644.5731	8 6 3	12.97	39.85	47.18
4644.4959	8 6 2	13.08	40.32	46.61
4761.7227	8 7 2	13.42	81.29	5.29
4761.7227	8 7 1	13.42	81.29	5.29
4898.5115	8 8 1	5.98	92.78	1.24
4898.5115	8 8 0	5.98	92.78	1.24



**Fig. 4.** The comparison of self-broadening coefficients  $\gamma$  of  $D_2^{16}O$  molecule calculated for the line of  $\nu_1 + \nu_2$  ( $J_f = 8$ ) band taking (black dots) and not taking (white dots) into account the influence of accidental resonances.



**Fig. 5.** The comparison of self-shifting coefficients  $\delta$  of  $D_2^{16}O$  molecule calculated for the line of  $\nu_1 + \nu_2$  ( $J_f = 8$ ) band taking (black dots) and not taking (white dots) into account the influence of accidental resonances.

As it is shown in Fig. 5, accidental resonances have a strong effect on the calculated values of self-shifting coefficients. The difference in the values of  $\delta$  coefficients obtained with and without accounting for accidental resonances can reach 100%. Figures 4 and 5 indicate a strong necessity of accounting for the accidental resonances in calculations of self-broadening and self-shifting coefficients for  $D_2^{16}O$  molecule.

## Modeling of $\gamma$ calculated values

As it was mentioned above, the calculations of  $\gamma$  and  $\delta$  coefficients at temperatures  $216 \leq T \leq 1200$  K were conducted for  $\nu_2$  band, aiming at modeling of the temperature dependence of the broadening coefficients  $\gamma$ .

Analytical formula for determination of  $\gamma$  coefficients, containing the fitting parameters defined from calculated and experimental values for  $\gamma$  were given in Refs. 3 and 12. One of them has a slight modification:

$$\gamma(K_i, K_f) = \gamma(\text{sur}) = x_1 + (x_2 + x_5(-1)^{J_i+K_i+K_{c,i}}) \times (1./\text{Ch}[x_3(K_i - x_4)] + 1./\text{Ch}[x_3(K_f - x_4)]), \quad (3)$$

in which

$$x_k = x_{k0} + x_{k1}(J_i + J_f) + x_{k2}(J_i + J_f)^2, \quad (4)$$

was used in this paper. The modification is connected with introduction of an additional term, containing the parameter  $x_5$ . This term takes into consideration the dependence of the self-broadening coefficient on the quantum number  $K_c$  of the initial rotational state. The temperature dependence of the parameter  $x_k$  has the form

$$x_k(J, T) = x_k(J, T_0)(T/T_0)^{n_k}, \quad (5)$$

in which  $x_k(J, T_0)$  is defined by relation (4). Usually, at slight changes of  $T$  the temperature dependence of  $\gamma$  is modeled as

$$\gamma(T) = \gamma(T_0)(T_0/T)^n. \quad (6)$$

The model parameters  $x_{k0}$ ,  $x_{k1}$ ,  $x_{k2}$ ,  $n_k$  ( $k = 1, \dots, 5$ ) were defined by the method of least squares from calculated values of  $\gamma$  and are presented in Table 2.

**Table 2. Parameters  $x_k(T_0)$  ( $T_0 = 296$  K) and  $n_k$  from formulas (3) and (4), which determine the temperature dependence of  $D_2^{16}O$  molecule self-broadening coefficients**

Parameter	Value	Parameter	Value
$x_{10}$	$0.1253 \pm 0.001$	$n_3$	$-0.34648 \pm 0.01214$
$n_1$	$-0.63916 \pm 0.02123$	$x_{40}$	$-0.6066 \pm 0.0396$
$x_{20}$	$0.2216 \pm 0.0022$	$x_{41}$	$0.1867 \pm 0.0012$
$x_{21}$	$-(0.1348 \pm 0.0162) \cdot 10^{-2}$	$n_4$	0.0
$x_{22}$	$-(0.3196 \pm 0.0271) \cdot 10^{-4}$	$x_{50}$	0.0
$n_2$	$-0.77932 \pm 0.00743$	$x_{51}$	$(0.6234 \pm 0.0378) \cdot 10^{-3}$
$x_{30}$	$0.2116 \pm 0.0120$	$n_5$	$-2.0427 \pm 0.0646$
$x_{31}$	$0.01219 \pm 0.0008$		
$x_{32}$	$-(0.1820 \pm 0.0141) \cdot 10^{-3}$		

Note. Parameters  $x_{10}$ ,  $x_{20}$ ,  $x_{21}$ ,  $x_{30}$  have  $cm^{-1} \cdot atm^{-1}$  dimensionality, other parameters are dimensionless.

The quality of determination of  $\gamma$  coefficients by analytical formula  $\gamma(sur)$  (3) is the same as in the case of the main isotopic modification.<sup>12</sup> About 90% of all values of  $\gamma$  are retrieved using  $\gamma(sur)$  (3) model with an accuracy of 20% as compared to the values of  $\gamma$  calculated by formulas (1) and (2); about 8.5% are retrieved with an accuracy of 40% and about 1.5% of  $\gamma$  values are retrieved with an accuracy between 40 and 50%.

### Conclusion

The obtained parameters of  $\gamma(sur)$  analytical model (3) can be used for calculation of  $\gamma$  self-broadening coefficients of  $D_2^{16}O$  absorption lines in a wide interval of rotational quantum numbers ( $J, K_a \leq 25$ ) and temperatures, as well as for study of molecule spectra in other spectral ranges. The influence of accidental results on calculated values of  $\gamma$  and  $\delta$  coefficients is thoroughly estimated. These results strongly influence the values of self-shifting coefficients (Fig. 5).

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