Calculations of self-broadening and self-shift of water vapor spectral lines with the use of accurate vibration-rotation wave functions

N.N. Lavrent'eva,[1] T.P. Mishina,[1] L.N. Sinitsa,[1] and J. Tennyson[2]

[1] *V.E. Zuev Institute of Atmospheric Optics,*
Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia
[2] *Department of Physics and Astronomy, University College London, UK*

Received September 8, 2008

Self-broadening and self-shift coefficients of vibration-rotation lines of water molecules are calculated using a semi-empirical method. The method is based on the impact theory of broadening, modified through including additional parameters, obtained by involving empirical data. Model parameters are determined by fitting the broadening and shift coefficients to experimental data. The calculations are made using anharmonic wavefunctions, determined by the variational method. This approach takes into account contributions of all scattering channels, induced by collisions of molecules. The calculation results well agree with experimental data.

Introduction

The coefficients of water vapor line broadening and shift induced by the pressure of N_2, O_2, H_2O, as well as other atmospheric gases, are of interest to many atmospheric applications and, in particular, to atmospheric laser sensing problems. The availability of many precise measurements of water vapor line parameters in microwave, IR, and visible spectral range[1–4] makes it possible to check and further improve the impact theory of the spectral line broadening. More exact calculations of half-widths and shifts of water vapor line centers require the development of semi-classical Robert–Bonamy theory,[5] being presently the main calculation method. Apart from revising and refining the general formulae of the theory, it is necessary to know exact wavefunctions, energy levels, and collision-induced transition probabilities. It should be noted that the majority of previous works,[6–10] used the wavefunctions determined by the method of effective rotational Hamiltonians.

In this paper, we estimate the inter-molecular effects on line broadening and shift with the help of exact vibration-rotation wavefunctions, calculated by the variational method, describe the theoretical foundations, and present certain details of line profile calculations. In addition, we present the results of calculations and discuss their comparison with experimental data.

1. Basic formulas and calculation details

For calculation of vibration-rotation spectrum of triatomic molecules, modelers have developed a number of methods, which use the direct solution of the Schrödinger equation. These methods can ensure the accuracy close to the experimental one. The quality of these calculations is determined predominately by the quality of potential energy surface, which in most cases involves the Born–Oppenheimer approximation. For our calculations, we also need the matrix elements of the dipole transition moment, which are calculated using dipole moment surface. The best is the Partridge–Schwenke surface,[11] obtained from *ab initio* calculations.

For the calculations, we use the energy levels and dipole moments from the BT2 list.[12] The BT2 line list contains all the transitions between the vibration-rotation states of water up to 30 000 cm^{-1} (221 000 states, 5.08×10^8 transitions), for which the rotation quantum numbers reach $J = 50$.

For calculations of coefficients of water molecule spectral line broadening and shift, induced by the pressure of different atmospheric gases, we used a semiempirical method, similar to the Anderson–Tsao–Curnutte (ATC) approach.[3,14] This method works in the framework of the impact theory approximations. General assumptions in this case are as follows: the collisions are binary, their lengths are shorter than the inter-collision times, and the translational particle motion is described by the classical-trajectory approximation, with the line interference disregarded. The semiempirical method is described in Ref. 15 in detail, and only its outline is given here.

According to the general considerations of the semiclassical theory, the halfwidth γ_{if} and shift of line center δ_{if} of the transition $i \rightarrow f$ can be written as follows:

$$\gamma_{fi} + i\delta_{fi} = \frac{n}{c}\sum_p \rho(p)\int_0^\infty vf(v)\mathrm{d}v\int_0^\infty bU(i,f,p,b,v)\mathrm{d}b. \qquad (1)$$

© 2008 Institute of Atmospheric Optics

The efficiency function $U(i,f,p,b,v)$ has the form

$$\begin{aligned} &\mathrm{Re}\,U(i,f,p,b,v) = 1 - \{1 - S^{\mathrm{L}}_{2,fp,ip}\} \times \\ &\times \cos[S_{1,fp} - S_{1,ip} + \mathrm{Im}\,S_{2,fp} - \mathrm{Im}\,S_{2,ip}] \times \\ &\times \exp[-(\mathrm{Re}\,S_{2,fp} + \mathrm{Re}\,S_{2,ip} + S^{\mathrm{C}}_{2,fp,ip})]; \\ &\mathrm{Im}\,U(i,f,p,b,v) = \{1 - S^{\mathrm{L}}_{2,fp,ip}\} \times \\ &\times \sin[S_{1,fp} - S_{1,ip} + \mathrm{Im}\,S_{2,fp} - \mathrm{Im}\,S_{2,ip}] \times \\ &\times \exp[-(\mathrm{Re}\,S_{2,fp} + \mathrm{Re}\,S_{2,ip} + S^{\mathrm{C}}_{2,fp,ip})]. \end{aligned} \tag{2}$$

Here, n is the density of perturbing particles; $\rho(p)$ is the population of the level p; p is the set of quantum numbers of the second (perturbing) molecule; v is the relative velocity of colliding molecules; $f(v)$ is the Maxwell velocity distribution function; b is the impact distance; S_1 and S_2 are the first- and second-order expressions in terms of the perturbation theory; indices L and C correspond to the "linked" and "connected" diagrams of the perturbation theory. The first-order term S_1 is responsible for the adiabatic effect and is determined only by the isotropic part of the potential, while S_2 is governed by its anisotropic part. Both functions depend on the "classic" trajectory of the relative motion of colliding molecules.

Expressions (1) and (2) depend on forces of dipole transitions $D^2(ii'|l)$ and $D^2(ff'|l)$ of different scattering channels $i \to i'$, $f \to f'$, tying the lower and upper transition levels with other closely lying levels. These parameters are squares of reduced matrix elements of molecular constants, such as dipole moment or components of quadrupole tensor. The parameters of line profile in the Anderson theory are expressed as follows:

$$\gamma_{if} = A(i,f) + \sum_{i'} D^2(ii'|l)P_l(\omega_{ii'}) + \sum_{f'} D^2(ff'|l)P(\omega_{ff'}) + \ldots, \tag{3}$$

$$\delta_{if} = B(i,f) + \sum_{i'} D^2(ii'|l)P_l(\omega_{ii'}) + \sum_{f'} D^2(ff'|l)P(\omega_{ff'}) + \ldots,$$

higher-order terms are neglected here. The formula

$$P_l(\omega) = \frac{n}{c}\sum_p \rho(p) \sum_{l',p'} A_{ll'} D^2(pp'|l') \times \times F_{ll'}\left(\frac{2\pi c b_0(p,i,f)}{v}(\omega + \omega_{pp'})\right) \tag{4}$$

represents the efficiency function of scattering channels $i \to i'$ or $f \to f'$ (if $\omega_{ii'}$ and $\omega_{ff'}$ are replaced by ω). Formula

$$A(i,f) = \frac{n}{c}\sum_p \rho(p) \int_0^\infty v F(v) b_0^2(v,p,i,f)\,\mathrm{d}v$$

represents the usual summand of the Anderson theory, stipulated by the interruption ($b_0(v,p,i,f)$ is the interruption parameter);

$$B(i,f) = \frac{n}{c} B_1\{\alpha_2(\mu_f^2 - \mu_i^2) + 3\varepsilon\varepsilon_2(\alpha_f - \alpha_i)/[2(\varepsilon + \varepsilon_2)]\} \times \times \sum_p \rho(p) \int_0^\infty v F(v) b_0^{-3}(v,p,i,f)\,\mathrm{d}v$$

is the contribution of the isotropic part of potential; α, μ, and ε are the polarizability, dipole moment, and ionization potential of the water molecule, respectively; α_2 and ε_2 are the polarizability and the ionization potential of the perturbing molecule; $B_1 = -3\pi/(8\hbar v)$; $A_{ll'}$ are parameters for the determined ll-type of interaction; $l = 1$ corresponds to the dipole transitions, and $l = 2$ corresponds to quadrupole transitions in the absorbing molecule.

The transition probabilities $D^2(ii'|l)$ and $D^2(ff'|l)$ refer to the scattering channels $i \to i'$, $f \to f'$, and they depend only on the properties of the absorbing molecule. The efficiency function $P_l(\omega_{ii'})$ depends on the intermolecular potential, the trajectory of the relative molecule motion, energy levels, and wavefunctions of the buffer molecule. As Bykov et al.[15] suggested, the efficiency function $P_l(\omega)$ can be represented as:

$$P_l(\omega) = P_l^{\mathrm{A}}(\omega) C_l(\omega), \tag{5}$$

where $P_l^{\mathrm{A}}(\omega)$ is the efficiency function in the Anderson theory; $C_l(\omega)$ is the correction factor, which is determined from the fitting to the experimental data. Whereas the function $P_l^{\mathrm{A}}(\omega)$ determines all major contributions to the broadening, the factor $C_l(\omega)$ gives a small correction associated with accounting for certain fine effects. Calculations of line profile parameters for the case of H_2O–N_2, O_2, H_2O were made using the correction factor, representing the j-dependent function:

$$P_l(\omega_{ff'}) = P_l^{\mathrm{A}}(\omega_{ff'})[c_1/(c_2\sqrt{j_f} + 1)], \tag{6}$$

where c_1 and c_2 are the fitting parameters. The form of the correction factor for $P_l(\omega_{ii'})$ is analogous to formula (6) with index f replaced by i.

The effective dipole polarizability in the upper vibration state was defined in Ref. 18. The calculations were made with parameters $c_1 = 1.23$ and $c_2 = 0.08$. The best agreement of the calculations with experimental values is achieved by varying the model parameters for three J intervals (Tables 1 and 2).

Table 1. Root-mean-square deviation. Fitting parameters: $c_1 = 1.23$, $c_2 = 0.08$, and $R_0 = 7.76$ is the gas kinetic diameter

V_1 V_2 V_3	RMSγ*	RMSδ*
3 0 1	0.006	0.00354
2 2 1	0.00555	0.005052
0 0 1	0.006223	–

* RMS is the root-mean-square deviation.

Table 2. Root-mean-square deviation in the case of separating the calculation with respect to J values and varying the model parameters c_1, c_2, and gas kinetic diameter R_0

$V_1\ V_2\ V_3$	J	R_0, Å	c_1	c_2	RMSγ	R_0, Å	c_1	c_2	RMSδ
3 0 1	$J < 4$	7.76	1.23	0.08	0.00949	7.76	1.23	0.08	0.00628
		10.0	1.5	0.1	0.00814	10.0	1.1	0.1	0.00453
	$3 < J < 6$	7.76	1.23	0.08	0.00616	7.76	1.23	0.08	0.00657
		7.76	1.25	0.1	0.00629	9.0	0.5	0.1	0.00277
	$J > 5$	7.76	1.23	0.08	0.01484	7.76	1.23	0.08	0.00419
		9.0	1.1	0.25	0.00911	10.0	1.1	0.1	0.00285
2 2 1	$J < 4$	7.76	1.23	0.08	0.00942	7.76	1.23	0.08	0.00733
		10.0	1.23	0.1	0.0071	10.0	1.23	0.1	0.00619
	$3 < J < 7$	7.76	1.23	0.08	0.00712	7.76	1.23	0.08	0.00567
		7.76	1.25	0.1	0.00706	7.76	1.25	0.1	0.00561
	$J > 6$	7.76	1.23	0.08	0.01796	7.76	1.23	0.08	0.01510
		7.76	1.1	0.1	0.0164	7.76	1.25	0.1	0.01479
0 0 1	$J < 4$	7.76	1.23	0.08	0.01264				
		9.0	1.8	0.0	0.01618				
	$3 < J < 7$	7.76	1.23	0.08	0.00716				
		7.76	1.5	0.1	0.0074				
	$J > 6$	7.76	1.23	0.08	0.01153				
		9.0	1.5	0.08	0.01062				

2. Results and discussion

Earlier, the above semiempirical method and the method of effective Hamiltonians were applied to calculation of line profile parameters and coefficients of their temperature dependence in the case of colliding molecules H_2O–N_2, H_2O–O_2, CO_2–N_2, and CO_2–O_2.[9, 10, 16, 17] The results of these calculations were included in the carbon dioxide spectroscopic data bank[18] and in the ATMOS information system,[19] freely available from internet.

In the present paper, the semiempirical method is supplemented with the use of exact variational wavefunctions for the calculation of self-broadening and self-shift of water vapor lines. In principle, the use of the exact wavefunctions, obtained from global variational calculations, widens the applicability limits to the level of the molecule dissociation.

The major contribution to the line self-broadening and self-shift is made by the dipole-dipole interaction. We also take into account the higher-order electrostatic interactions and polarization (induction and dispersion) interactions. The interruption procedure is applicable to molecules, characterized by strong interactions, when the radius of the closest approach of molecules is less than the interruption parameter, i.e., $r_c < b_0$, where r_c is the radius of the closest approach, and b_0 is the interruption radius. The interaction of two strong dipoles (H_2O–H_2O) ensures the fulfillment of the condition $r_c < b_0$; the influence of short-range forces is weak in this case and is accounted for via the correction factor.

To take into account the contributions of different scattering channels, corresponding to collisional transitions, we used the transition probabilities $D^2(ii'|l)$ and $D^2(ff'|l)$, reconstructed from Einstein coefficients in the line list BT2. It was necessary to select the Einstein coefficients from 500 millions of values, presented in the full BT2 list. In the calculation of line broadening and shift parameters, we took into account the scattering channels, induced by collisions and acceptable with respect to symmetry. In the present approach, they are much more abundant than in the case of the use of standard Watson Hamiltonian. We have found in the calculations that the contributions of the scattering channels with $\omega_{ii'} > 700\ \text{cm}^{-1}$ and $K_a - K'_a > 3$ can be neglected.

First of all, we performed test calculations for detailed analysis of factors, determining the variations of line broadening and shift coefficients. Then, we performed mass calculations of self-broadening and self-shift coefficients of water vapor lines for $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_2 + \nu_3$, and ν_3 vibration-rotation bands, presented in the experiments.[1, 20] All calculations were made for the temperature $T = 297$ K.

Figure 1 presents the calculated and experimental self-broadening coefficients for three water vapor bands (N is the number of vibration-rotation transitions).

It is seen that the calculations are in satisfactory agreement with the experiment. For all three bands, RMS does not exceed 0.007 cm^{-1}/atm. The self-broadening coefficients of water vapor lines, calculated with the same set of fitting parameters for all bands, reasonably well correlate with experimental values.

To achieve a better correspondence, we separated the data with respect to rotation quantum number, that is, we sought the parameters separately for small, medium, and high J. As an example, figure 2*a* presents the results, obtained with different sets of fitting parameters for high J. The parameters for medium values are the same as for the whole band.

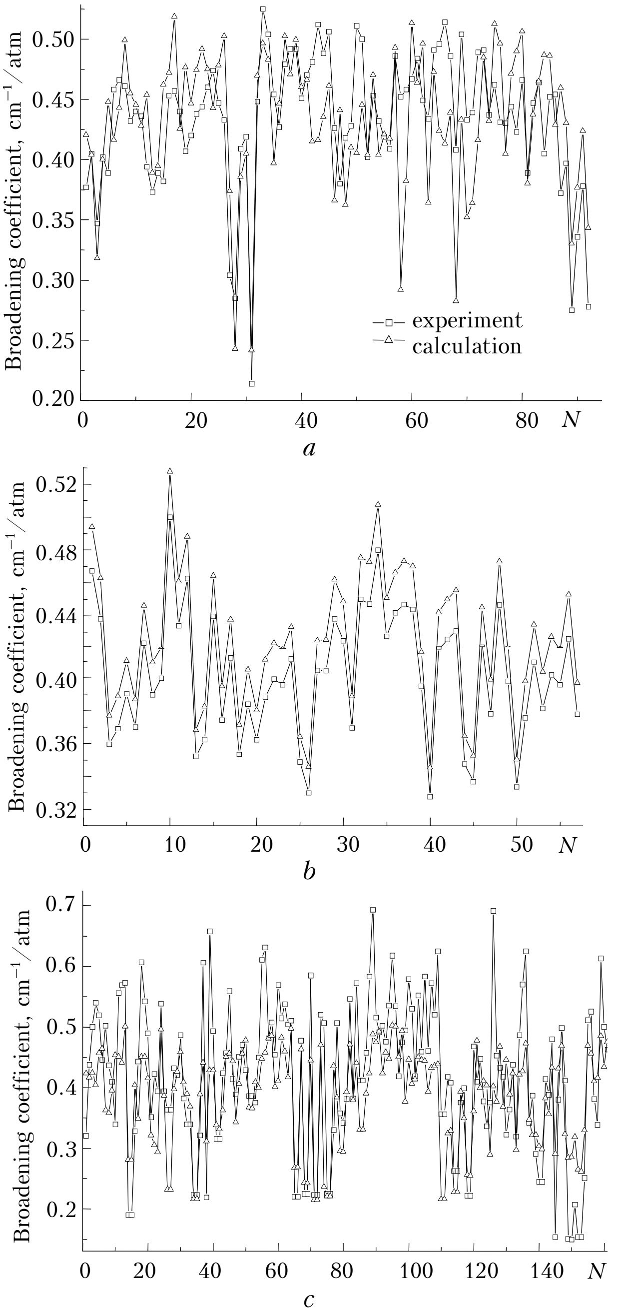

Fig. 1. Calculated and experimental water line self-broadening coefficients: band $3\nu_1 + \nu_3$ (*a*); band $2\nu_1 + 2\nu_2 + \nu_3$ (*b*); band ν_3 (*c*); experiment[1] (*a*, *b*) and data reproduced from Ref. 20 (*c*).

The calculations of spectral line self-shift coefficients of water molecules are presented in Fig. 2*b*; the values for the calculated lines vary from -0.09 to 0.06 cm$^{-1}\cdot$atm^{-1}. Note that the line self-shift coefficient increases by almost an order of magnitude in comparison with line shift induced by the pressure of non-polar molecules of the type of nitrogen or oxygen. The calculated self-shift coefficients, like the self-broadening coefficients, well correlate with experimental values. The water vapor lines with a large vibration quantum number are shifted by water vapor in a different way than by nitrogen or oxygen. Whereas nitrogen- or oxygen-induced line shift is always negative for large V, which is determined by the predominance of induction-type interaction, the water vapor line self-shift may be both negative and positive. This is because of the increase of the role of electrostatic interaction of colliding molecules: two strong dipoles interact in the H_2O–H_2O system.

Thus, the presented method makes it possible to calculate the parameters of water line shape in the case of self-broadening up to the dissociation limit. The results, obtained by this method, are nearly as accurate as experimental.

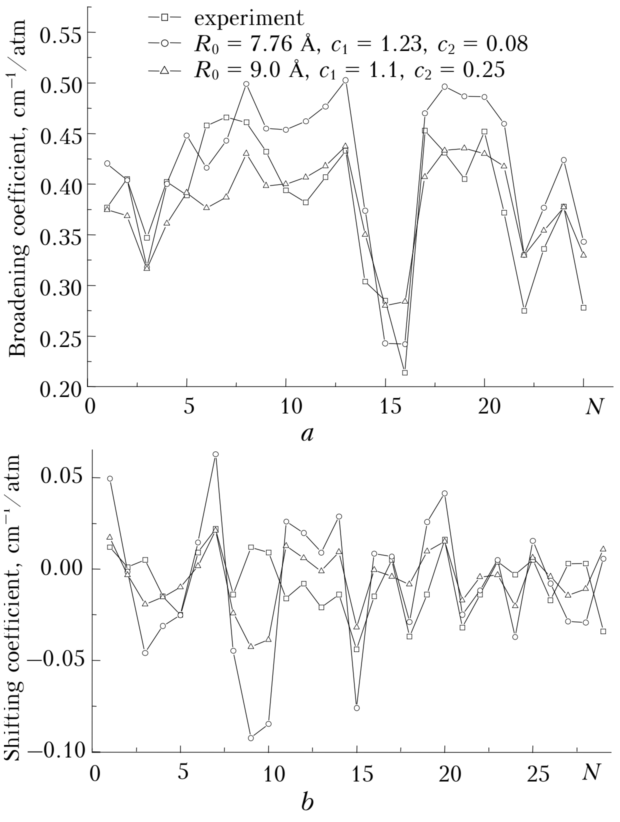

Fig. 2. Calculated and experimental self-broadening coefficients for high J values (*a*), self-shift coefficients for medium J values (*b*) for the band $3\nu_1 + \nu_3$ [Ref. 1]. R_0 is the gas kinetic diameter, Å.

Acknowledgements

This work is supported by the Russian Foundation for Basic Research (Grant 08-02-12061-ofi) and the Grant of the Great Britain Royal Society (No. 2006/R3 IJP).

References

1. B.E. Grossman and E.V. Browell, J. Mol. Spectrosc. **136**, 264–294 (1989).
2. J.-P. Chevillard, J.-Y. Mandin, J.-M. Flaud, and C. Camy-Peyret, Can. J. Phys. **69**, No. 10, 1286–1298 (1991).

3. K.M.T. Yamada, M. Harter, and T. Giesen, J. Mol. Spectrosc. **157**, 84–94 (1993).
4. R.A. Toth, J. Mol. Spectrosc. **201**, No. 2, 218–243 (2000).
5. D. Robert and J.J. Bonamy, J. de Phys. **40**, No. 10, 923–943 (1979).
6. R. Lynch, R.R. Gamache, and S.P. Neshyba, J. Chem. Phys. **105**, 5711–5721 (1996).
7. R.R. Gamache, R. Lynch, J.J. Plateaux, and A. Barbe, J. Quant. Spectrosc. and Radiat. Transfer **57**, No. 4, 485–496 (1997).
8. A. Valentin, Ch. Claveau, A. Bykov, N. Lavrentieva, V. Saveliev, and L. Sinitsa, J. Mol. Spectrosc. **198**, 218–229 (1999).
9. V. Zéninari, B. Parvitte, D. Courtois, N.N. Lavrentieva, Yu.N. Ponomarev, and G. Durry, Mol. Phys. **102**, 1697–1706 (2004).
10. C. Camy-Peyret, A. Valentin, Ch. Claveau, A. Bykov, N. Lavrentieva, V. Saveliev, and L. Sinitsa, J. Mol. Spectrosc. **224**, 164–175 (2004).
11. H. Partridge and D.W. Schwenke, J. Chem. Phys. **106**, No. 11, 4618–4639 (1997).
12. R.J. Barber, J. Tennyson, G.J. Harris, and R.N. Tolchenov, Mon. Notic. Roy. Astron. Soc. **368**, 1087–1094 (2006).
13. P.W. Anderson, Phys. Rev. **76**, No. 5, 657–661 (1949).
14. C.J. Tsao and B. Curnutte, J. Quant. Spectrosc. and Radiat. Transfer **2**, 41–91 (1962).
15. A. Bykov, N. Lavrent'eva, and L. Sinitsa, Mol. Phys. **102**, 1706–1712 (2004).
16. A.D. Bykov, N.N. Lavrentieva, T.P. Mishina, L.N. Sinitsa, R.J. Barber, R.N. Tolchenov, and J. Tennyson, J. Quant. Spectrosc. and Radiat. Transfer **3034**, 1–11 (2008).
17. S.A. Tashkun, V.I. Perevalov, J.-L. Teffo, A.D. Bykov, and N.N. Lavrentieva, J. Quant. Spectrosc. and Radiat. Transfer **82**, 165–196 (2003).
18. ftp://ftp.iao.ru/pub/CDSD-1000
19. http://saga.atmos.iao.ru
20. J.Y. Mandin, C. Camy-Peyret, J.-M. Flaud, and G. Guelachvili, Can. J. Phys. **60**, 94–101 (1982).