Temperature dependence of the H_2O absorption line broadening coefficients

A.D. Bykov and V.N. Stroinova*

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
** Tomsk Polytechnic University*

Received November 9, 2004

The temperature dependence of H_2O half-widths is analyzed. The H_2O half-widths calculated by the Anderson–Tsao–Curnutte technique within the temperature range $200 < T < 800$ K for lines belonging to four ro-vibrational bands are presented. The temperature coefficients for H_2O half-widths are calculated.

Introduction

Studying the temperature dependence of absorption line half-widths of atmospheric gases is of great significance from the viewpoint of various applications of atmospheric optics.

First, the temperature dependence of relaxation parameters of a line profile is quite significant when investigating the flame spectra.

Second, under atmospheric conditions the temperature varies widely – from 120 to 350 K [Refs. 1–3] as a function of altitude, which should be taken into account when calculating the atmospheric transmission functions. For example, in sensing the atmosphere along vertical and slant paths, it is important to know the dependence of a line half-width on altitude and, consequently, on temperature.

Third, water vapor and carbon dioxide are the major greenhouse gases, influencing the global climate change on the Earth,[2] and therefore it is necessary to study the temperature dependence of half-widths and shifts of H_2O and CO_2 lines by the pressure of different buffer gases.

Fourth, nowadays the databases of spectroscopic parameters (for example, HITRAN,[4] CDSD-1000[5]) are compiled, which should include the calculated values of half-widths at the increased temperature and the coefficients of the temperature dependence of half-widths.

The aim of this work is to analyze the temperature dependence of half-widths of H_2O lines caused by transitions to high vibrational states. The H_2O line half-widths are calculated within the framework of the semiclassical impact theory (Anderson–Tsao–Curnutte (ATC) technique), along with the coefficients of their temperature dependence for several tens of lines belonging to $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_2 + \nu_3$, $2\nu_1 + 2\nu_3$, and ν_2 bands in the cases of self-broadening and broadening induced by the pressure of air, nitrogen, and oxygen.

1. Analysis of temperature dependence of the line half-width

Within the ATC technique, a line half-width γ_{if} is defined as follows:

$$\gamma_{if}(b,v) = \frac{n}{c}\sum_j \rho(j)\int_0^\infty F(v)v\,\mathrm{d}v\left[\frac{b_c^2}{2} + \int_{b_c}^\infty S_2(b)b\,\mathrm{d}b\right]. \quad (1)$$

Here i, f are the sets of vibrational and rotational quantum numbers of the initial and final states of a transition; n is the concentration of perturbing (buffer) particles; c is the speed of light; $\rho(j)$ is the population of the jth level of the perturbing molecule; $F(v)$ is the Maxwell distribution for the relative velocity of colliding particles; b_c is the interruption parameter; $S_2(b)$ is the Anderson interruption function for collision with the impact parameter b and the relative velocity v. The interruption function for collisions of a polar molecule with a non-polar one (for example, H_2O with N_2) is determined mostly by the dipole-quadrupole term of the electrostatic part of the intermolecular potential:

$$S_2(b) = \frac{4}{45}\frac{1}{(hvb^3)^2}\sum_j D(jj' \mid 2)\times$$

$$\times\left\{\sum_{i'} D(ii' \mid 1)\varphi(k_{ii'jj'}) + \sum_{f'} D(ff' \mid 1)\varphi(k_{ff'jj'})\right\}. \quad (2)$$

Here $D(jj'|2)$ are the strengths of quadrupole transitions in the N_2 molecule; $D(ii'|1)$; $D(ff'|1)$ are the strengths of the dipole transitions in the H_2O molecule.

The resonance function $\varphi(k_{ii'jj'})$ depends on the resonance parameter $k_{ii'jj'}$, determined by the parameters of collision b and v:

$$k_{ii'jj'} = \frac{2\pi cb}{v}(E_i - E_{i'} + E_j - E_{j'}), \quad (3)$$

where $E_i - E_{i'}$, $E_j - E_{j'}$ are the differences between energy levels of virtual transitions in the absorbing and perturbing molecules.

The temperature dependence of γ_{if} in Eqs. (1)–(3) is a complex function, which is difficult to be written in the explicit form. Actually, the impact parameter b_0, determined from the solution of the interruption equation, is an implicit, slowly varying function of temperature. The resonance function contributes differently to the half-width at different temperatures because of the implicit dependence of the resonance parameter on temperature. It is also important to take into account the explicit temperature dependence of the half-width (1). It becomes necessary to perform the general analysis of the temperature dependence of γ_{if}. The concentration of buffer particles n, mean relative velocity v, and population of the jth level $\rho(j)$ explicitly depend on temperature T:

$$n = \frac{n_0}{T};\; v = \sqrt{\frac{8kT}{\pi m}};$$
$$\rho(j) = \frac{(2j+1)l}{\rho_0}\exp\left(\frac{-E_j}{kT}\right), \tag{4}$$

where k is the Boltzmann constant; m is the reduced mass of colliding particles; E_j is the energy of the jth level of the perturbing molecule; $(2j + 1)l$ is the partition function; $\rho_0 = \sum_j \exp\{-E_j/kT\}$. Besides the explicit temperature dependence of the half-width (1), there is implicit dependence. Introduce a slowly varying functions of temperature $A(T)$ and $B(T)$, describing the implicit temperature dependence of $\mathrm{Re}S_2(b)$ [Eq. (2)]:

$$A(T) = \alpha\sum_j \rho(j) b_0^2(j,T);$$

$$B(T) = \beta\sum_j \rho(j) b_0^{-4}(j,T)\sum_{j'} D(jj'\,|\,2)\times$$
$$\times\left\{\sum_{i'} D(ii'\,|\,1)\varphi\left(\frac{2\pi c b(j,T)\omega_{ii'ff'}}{v}\right) + (i \to f)\right\}. \tag{5}$$

Here α and β are constants, including the molecular constants and independent of temperature; D is the generalized line strength; φ is the real part of the resonance function for the case of dipole-quadrupole interaction; $A(T)$, $B(T) > 0$. Separating the explicit temperature dependence of the half-width from Eq. (1) and taking into account Eq. (4), we can write:

$$\gamma_{if}(T) = \frac{A(T)}{T^{1/2}} + \frac{B(T)}{T^{3/2}}. \tag{6}$$

In Ref. 6, the power-law approximation of the temperature dependence of the half-width was proposed:

$$\gamma(T) = \gamma(T_0)(T_0/T)^N, \tag{7}$$

where $T_0 = 300$ K; N is the coefficient of temperature dependence of the half-width. If the coefficient N is determined for some line in the temperature range $(T + \Delta T)$ experimentally or by calculation, then Eq. (7) allows the half-width $\gamma(T_1)$ to be reconstructed beyond the range $(T + \Delta T)$. In Ref. 7, it was proposed to use the exponential approximation of the temperature dependence of the half-width in place of the ordinary power-law approximation (7).

The resonance conditions $k_{ii'jj'}$, $k_{ff'jj'} = 0$ for the most populated levels of the absorbing molecule exert a significant influence on the line half-width. At the exact resonance, $k = 0$, $\varphi = 1$, and the line half-width has the maximum value. Under conditions of exact resonance, the impact parameter depends on temperature as $T^{-1/6}$, and $\gamma_{ij} \approx T^{-1/6}$. Another limiting case is associated with the absence of resonance, when the impact parameter is independent of temperature and $\gamma_{ij} \approx T^{-1/2}$. In the intermediate cases, when $k_{ii'jj'}$, $k_{ff'jj'} > 0$, the temperature dependence of the line half-width is determined by two-term equations (5)–(6). The analysis shows that the line half-width decreases gradually with temperature.

2. Results and discussion

In this work, we have calculated the temperature dependence of the half-width of H_2O lines belonging to the ν_2 band under conditions of self-broadening. Figure 1 shows the calculated results in comparison with the experimental data.[8] It can be seen from Fig. 1 that the calculated line half-widths well agree with the experimental ones accurate to the experimental uncertainty for the temperature $250 < T < 600$ K.

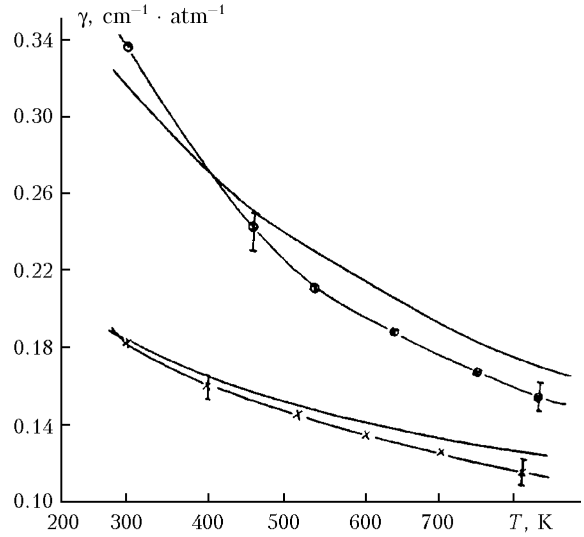

Fig. 1. Temperature dependence of half-widths for lines belonging to the ν_2 band of H_2O in the case of self-broadening: experimental[8] 7_{70}–8_{81} (×) and 8_{63}–9_{72} ( ); calculation (—).

At $T < 250$ K the calculated half-widths appear to be underestimated as compared to the experimental ones, while at $T > 600$ K they are, on the contrary, overestimated. It has been found that the increase of temperature from 250 to 600 K leads to the narrowing of the 7_{70}–8_{81} line by 10% and 8_{63}–9_{72} line by 25%. The calculated value of the coefficient N in the temperature dependence of the line half-width (7) was found to be 0.41 for the 8_{63}–9_{72} line and 0.37 for the 7_{70}–8_{81} line in the temperature range $250 < T < 600$ K. It should be noted that the values of N differ for different lines of the ν_2 band and do not coincide with the recommended value $N = 0.59$ [Ref. 6].

The calculated H_2O line half-widths in the case of air pressure induced broadening for some lines of the $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_2 + \nu_3$, and $2\nu_1 + 2\nu_3$ bands are tabulated below along with the coefficients of the temperature dependence N.

Coefficients N_{exp} (experiment[9,10]) and N_{calc} (this work) of temperature dependence of H_2O line half-widths

$J\ K_a\ K_c \rightarrow J'\ K'_a\ K'_c$	N_{exp}	N_{calc}
	$3\nu_1 + \nu_3$ band	
5_{32}–4_{31}	0.64	0.68
5_{23}–4_{22}	0.79	0.72
5_{14}–4_{13}	0.75	0.69
5_{24}–4_{23}	0.63	0.57
5_{05}–4_{04}	0.69	0.58
4_{13}–3_{12}	0.71	0.70
4_{23}–3_{22}	0.74	0.63
4_{14}–3_{13}	0.79	0.74
3_{21}–2_{20}	0.68	0.67
3_{12}–3_{11}	0.76	0.68
6_{16}–5_{15}	0.72	0.58
	$2\nu_1 + 2\nu_2 + \nu_3$ band	
2_{21}–2_{20}	0.77	0.72
5_{41}–5_{42}	0.52	0.55
3_{03}–4_{04}	0.62	0.63
4_{14}–3_{31}	0.70	0.68
4_{14}–5_{15}	0.61	0.63
5_{05}–6_{06}	0.53	0.60
2_{12}–3_{31}	0.80	0.77
	$2\nu_1 + 2\nu_3$ band	
5_{14}–6_{15}	0.59	0.56
4_{04}–3_{13}	0.75	0.74
5_{14}–4_{23}	0.61	0.65

It can be seen from the Table that the calculated and experimental[9,10] values of N are in a good agreement. The coefficient N_{exp} varies from 0.52 to 0.79, and the line half-width can decrease with temperature by 30% for the lines of the $3\nu_1 + \nu_3$ band. In Refs. 9 and 10 it was found that lines with low values of the rotational quantum number have small coefficients N. Figure 2 shows the calculated temperature dependence of half-widths of four lines belonging to the $3\nu_1 + \nu_3$ band in the case of air broadening. The coefficients N for these lines are given in the Table. Under the self-broadening conditions, the temperature dependence is stronger, and the coefficient N varies from 0.35 to 1.06. References 9 and 10 present the equations, whose coefficients are determined from fitting of the coefficients N to the experimental half-width values. The equations establish the relation between the half-width and coefficient of temperature dependence in the cases of self-broadening (N_1) and air broadening (N_2):

$$\begin{aligned} N_1 &= 3.24\gamma_{H_2O} - 0.68, \\ N_2 &= 9.31\gamma_{air} - 0.15. \end{aligned} \tag{8}$$

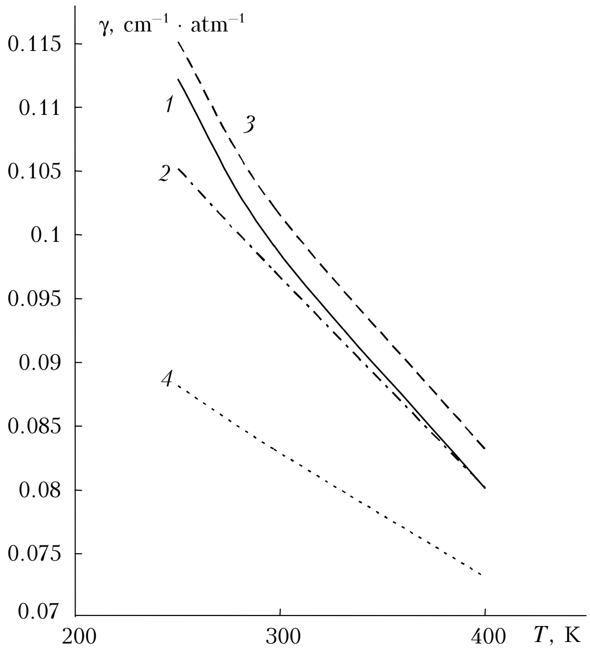

Fig. 2. Temperature dependence of line half-widths of the H_2O $3\nu_1 + \nu_3$ band in the case of air broadening: 5_{23} – 4_{22} line (*1*), 3_{21} – 2_{20} line (*2*), 4_{13} – 3_{12} line (*3*); and 6_{16} – 5_{15} line (*4*).

References 11–13 present H_2O and CO_2 line half-widths calculated at different temperatures by the Robert–Bonamy method in comparison with experimental data. The calculated coefficient of the temperature dependence is also in a good agreement with experimental N in the temperature range $160 < T < 600$ K. In this work and in Ref. 13, it has been found that at higher and lower temperatures both the ATC technique and the Robert–Bonamy method lead to large errors in the calculation of half-widths of H_2O and CO_2 lines with high values of the rotational quantum numbers and the power approximation (7) poorly reconstructs the line half-widths. At $T < 160$ K the calculated results are underestimated as compared with the experimental data, while at $T > 600$ K they are, on the contrary, overestimated.

Conclusions

In this paper, we have calculated the half-widths for lines of the H_2O ν_2, $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_2 + \nu_3$, and $2\nu_1 + 2\nu_3$ bands in the cases of self-broadening and broadening induced by pressure of air and nitrogen. The half-width calculated by the ATC technique have been compared with the experimental data. This comparison and the analysis of calculations by the Robert–Bonamy method have shown that the power approximation of the temperature dependence of the half-width allows correct reconstruction of this temperature dependence in the range $200 < T < 600$ K for moderate values of the quantum number J. It has been found that the ATC technique, which carefully accounts for the intramolecular interactions and the vibrational effect, allows the correct calculation of H_2O line half-widths in the temperature range $200 < T < 600$ K.

References

1. V.E. Zuev and V.S. Komarov, *Statistical Models of Temperature and Gaseous Constituents of the Atmosphere* (Gidrometeoizdat, Leningrad, 1986), 172 pp.
2. V.E. Zuev and G.A. Titov, *Atmospheric Optics and Climate* (IAO SB RAS, Tomsk, 1996), 271 pp.
3. G. Anderson, S. Clough, F. Kneizys, J. Chetwynd, and E. Shettle, *AFGL Atmospheric Constituent Profiles* (0–120 km), Air Force Geophysics Laboratory, AFGL-TR-86-0110, Environ. Res. Paper, No. 954 (2001), 25 pp.
4. L.S. Rothman, D. Jacquemart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian, Jr., K. Chance, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, and G. Wagner, J. Quant. Spectrosc. Radiat. Transfer (2004) (accepted).
5. S.A. Tashkun, V.I. Perevalov, J.L. Teffo, A.D. Bykov, and N.N. Lavrentieva, J. Quant. Spectrosc. Radiat. Transfer **82**, 165–196 (2003).
6. W.S. Benedict and L.D. Kaplan, J. Chem. Phys. **30**, 388–399 (1959).
7. R.R. Gamache and L.S. Rothmann, J. Mol. Spectrosc. **128**, 360–369 (1988).
8. A. Bauer, M. Godon, M. Kneddar, et al., J. Quant. Spectrosc. Radiat. Transfer **37**, 531–539 (1987).
9. B.E. Grossmann and E.V. Browell, J. Mol. Spectrosc. **138**, 562–595 (1989).
10. B.E. Grossmann and E.V. Browell, J. Mol. Spectrosc. **136**, 264–294 (1989).
11. M. Godon and A. Bauer, Chem. Phys. Lett. **147**, 189–191 (1988).
12. M. Godon, A. Bauer, M. Kneddar, and J.-M. Hartmann, J. Quant. Spectrosc. Radiat. Transfer **41**, 49–54 (1989).
13. J. Buldyreva and M. Chrysos, J. Chem. Phys. **115**, 7436–7441 (2001).