

THE CALCULATION OF HALF-WIDTHS AND SHIFTS OF THE WATER VAPOR ABSORPTION LINES DUE TO THE PRESSURE OF SULPHUR DIOXIDE

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The halfwidths and shift coefficients of the line centers of water vapor due to the pressure of sulphur dioxide are calculated and compared with experimental data. The large values of the shift coefficients and the dependence of the shift sign on the rotational quantum numbers observed in the experiment are completely explained by the strong dipole-dipole interaction.

The calculations of the parameters of the lines — positions of centers, intensities, half-widths, and shifts, — are very important for the spectroscopic applications in the atmospheric optics. In order to create atlases of the parameters of the absorption lines of the atmospheric and pollutant gases, it is necessary to develop the techniques for calculating the line center shift coefficients due to the air pressure.

The calculated results have been previously published in Refs. 1–3 and they were in a satisfactory agreement with the experimental data on the line center shifts of water vapor due to the pressure of nonpolar molecules of N₂, O₂, and air in the middle IR and in the visible. The calculational method was based on the Anderson–Tsao–Curnutte–Frost (ATCF) impact theory⁴ and additionally took into account the effect of intramolecular interactions on the parameters of the line shape (namely, on the variation of the molecular parameters when the absorbing molecule was vibrationally excited, on the polarization part of the intermolecular potential, and on the averaging over the relative velocities of the colliding molecules). Using that method such a molecular parameter as the polarizability of the water vapor molecule in an excited vibrational state (we discuss here the rovibrational transitions) was determined by fitting the calculated shift of one or several lines in the band to the measured lineshift due to the air pressure. Hence, it is of doubtless interest to perform calculations based on the technique proposed in Refs. 1–3 for other buffer gases. In this paper we present the calculated coefficients of pressure broadening and shift coefficients of the water vapor lines by SO₂ molecule with large permanent dipole moment.

In the framework of the ATCF method, the half-width γ_{if} and the shift δ_{if} corresponding to the transition $i \rightarrow f$ are determined by the following formulas:

$$\gamma_{if} = i\delta_{if} = \frac{n}{c} \sum_j \rho(j) \sigma_{if}(j);$$

$$\sigma_{if}(j) = \int_0^\infty dv v F(v) \left[\frac{b^2}{2} + \int_{b_c}^\infty db b S_{if}(j, b, v) \right]. \quad (1)$$

Here n is the concentration of buffer gas molecules, v is the relative velocity of the colliding molecules, $F(v)$ is the Maxwell distribution function, b is the impact parameter, the "interruption" function $S_{if}(j, b, v)$ determines the efficiency of the collisions of such type in the case of line broadening and shift, and i and f are the quantum numbers of the initial and final states corresponding to this transition. In accordance with the ATCF method,

$$S_{if}(j, b, v) = S_1(b) + S_2(b). \quad (2)$$

The real part of the interruption function determines the half-width while the imaginary one does the line center shift. For the mixture H₂O–SO₂, it is sufficient to take into account the dipole-dipole interaction in the electrostatic part of the potential and the interaction of the dipole-induced dipole type in the polarization part of the potential. In so doing, we obtain

$$S_1(b) = -i \frac{3\pi}{8 \hbar v b^5} \left\{ \alpha_2 \left[2d_e(d_{v_i} - d_{v_f}) + \frac{3}{2} \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} (\alpha_{v_i} - \alpha_{v_f}) \right] + d_2 (\alpha_{v_i} - \alpha_{v_f}) \right\}; \quad (3)$$

$$S_2(b) = \frac{d_2^2}{(\hbar v b^2)^2} \sum_{j'} D(jj') \times \left[\sum_{i'} D(ii') \varphi_1(k_{ii'jj'}) + \sum_{f'} D(ff') \varphi_1(k_{ff'jj'}) \right], \quad (4)$$

where d_e , d_{v_i} , and d_{v_f} are the permanent dipole moment and the dipole moments of the initial and final vibrational states corresponding to this transition, α_{v_i} and α_{v_f} are the polarizabilities of H₂O, ϵ_1 is the ionization potential, $D(ii')$ and $D(ff')$ are the dipole forces corresponding to these lines, $\varphi_1(k)$ are the resonance functions,⁴ and k is the nonadiabaticity parameter:

$$k_{ii'jj'} = \frac{2\pi c b}{v} (\omega_{ii'} + \omega_{jj'}). \quad (5)$$

Here $\omega_{ii'}$ and $\omega_{jj'}$ are the frequencies of the dipole transitions. The parameters α_2 , ϵ_2 , and d_2 of the buffer molecule have the same meaning as for the water molecule.

The first and the third terms in Eq. (3) describe the induction interactions while the second term does the dispersion interaction. The interactions of the dipole-induced dipole type are taken into account in Eq. (3). Formula (4) describes the contribution of the dipole-dipole potential. To determine it, we must to calculate the average dipole moments, the frequencies, and the probabilities of the dipole transitions for both an H₂O molecule and a buffer molecule. Since the imaginary part of the nonadiabaticity function is odd, the virtual transitions associated with the energy increase

or decrease make contributions with opposite signs to the lineshift. At the same time, the dispersion interaction makes a negative contribution as a result of the increase in the polarizability of a molecule in the excited states, but the sign of the contribution of the induction part of the potential to the shift depends on the ratio of the dipole moments of the initial and final states. For the (010) state of water, this contribution is positive. The analysis of formulas (3) and (4) shows that the contribution of the dipole-dipole interaction to the lineshift is proportional to b^{-2} and exceeds the contribution of the polarization interactions ($\sim b^{-3}$) by at least an order of magnitude. For this reason, in contrast to the case of the shift due to pressure of the nonpolar molecules,^{1,3} the sign of the absorption line center shift of H₂O due to the pressure of polar molecules is determined by the sign of the frequencies ω corresponding to the transitions $i \rightarrow i'$ (or $f \rightarrow f'$) in a molecule of H₂O and $j \rightarrow j'$ in a buffer molecule (see Eq. (5)). The value of the shift is determined by the dipole moments of H₂O and of a buffer molecule and by the probabilities of the dipole transitions $D(ii')$ (or $D(ff')$) and $D(jj')$. It has been experimentally shown that shifts of H₂O with self-broadening exceed the shifts due to pressure of nonpolar molecules, while the signs of the shift coefficients with self-broadening may be both positive and negative.⁵

The calculations were performed for 22 lines of the ν_2 band, for which the experimental values of the shifts were available.⁶ The measurements were carried out using a Fourier-spectrometer at two pressures of the buffer gas, namely, 0.45 and 0.9 atm. The measurement accuracy was 0.01 cm⁻¹.atm⁻¹. The polarizabilities and the dipole moments for a number of vibrational states of water has been published in Ref. 3. For the calculation, the molecular constants for the states (000) and (010) of water were taken from Refs. 7 and 8 (the dipole moment, the rotational and centrifugal constants), the spectroscopic constants of the ground vibrational state of SO₂ – from Ref. 9, the dipole moment of SO₂ – from Ref. 10, and the rest of the parameters of the molecules – from a reference book.

There is a peculiarity in the calculations of the coefficients of broadening and shift due to pressure of heavy molecules, which is associated with the necessity of taking into account a great number of terms when summing over j according to formula (1). As a consequence of the fact that the rotational constants of SO₂ are small, the energy spectrum of the ground vibrational state is "dense", and it is necessary to sum up to large values of the quantum number j (in our case, up to $j = 90$, which corresponds to an account of 10 000 terms in the sum (1)). In each step over j in Eq. (1) we must solve the interruption equation, which requires much computation time. For this reason, in accordance with Ref. 11, we made use of the following approximation:

$$\gamma_{if} - i\delta_{if} \approx \frac{n}{c} \left[\sum_{j=0}^{j_{\max}} \rho(j) \delta_{if}(j) + \left(1 - \sum_{j=0}^{j_{\max}} \rho(j) \right) \sigma^{\max} \right], (6)$$

where σ^{\max} is the differential cross section of a collision, which corresponds to the minimum value of the interruption parameter. In the calculations we assumed that it was equal to the gas-kinetic radius for the investigated mixture H₂O – SO₂, while the summation was limited by $j \leq 20$.

The calculated results are given in Table II, while the molecular parameters employed for the calculations are presented in Table I.

TABLE I. The molecular and spectroscopic constants of H₂O and SO₂.

Parameter	Vibrational state	H ₂ O	SO ₂
d, D	000	1.859	1.59
	010	1.827	–
$\alpha \cdot 10^{-25} \text{ cm}^3$	000	14.69	37.89
	010	14.93	–
$\varepsilon \cdot 10^{-11} \text{ erg}$		2.018	1.977
Rotation* centri-	000	Ref. 7	Ref. 9
fugal constants	010	Ref. 7	Ref. 9
Nuclear	τ -even	1	1
statistical weight	τ -odd	3	0

TABLE II. The shifts and half-widths of the absorption lines of H₂O in the ν_2 band broadened by a pressure of SO₂ (cm⁻¹.atm⁻¹).

$(J K_a K_c)$ $(J K_a K_c)'$	$\omega_{ij}, \text{ cm}^{-1}$	σ_{ij}	γ_{ij}
1	2	3	4
6 2 5 5 1 4	1447.953	-0.116	0.239
		-0.133	0.203
3 2 1 2 1 2	1464.907	-0.127	0.364
		-0.121	0.372
6 1 5 5 2 4	1481.249	0.062	0.211
		0.071	0.204
5 0 5 4 1 4	1496.249	-0.006	0.154
		-0.002	0.155
4 3 2 4 2 3	1525.501	-0.066	0.169
		-0.061	0.154
3 3 1 3 2 2	1528.569	-0.055	0.182
		-0.056	0.161
5 2 3 5 1 4	1554.352	-0.127	0.344
		-0.126	0.310
2 0 2 2 1 1	1564.876	0.055	0.418
		0.078	0.546
1 1 0 1 0 1	1576.186	-0.110	0.563
		-0.107	0.646
1 0 1 1 1 0	1616.711	0.100	0.582
		0.117	0.647
1 1 1 2 0 2	1627.828	-0.064	0.436
		-0.063	0.532
3 1 2 3 2 1	1645.971	0.050	0.379
		0.053	0.454
2 1 2 2 2 1	1662.809	0.083	0.302
		0.073	0.270
4 2 3 4 3 2	1704.455	0.017	0.188
		0.024	0.173
1 1 1 2 2 0	1706.350	0.033	0.385
		0.044	0.433
7 0 7 7 1 6	1723.487	-0.077	0.169
		-0.054	0.163
6 2 5 7 1 6	1756.819	-0.072	0.158
		-0.090	0.119
5 1 4 6 2 5	1761.829	0.088	0.278
		0.119	0.257
6 1 5 7 2 6	1775.634	0.088	0.241
		0.098	0.256
7 1 6 8 2 7	1790.952	0.061	0.172
		0.060	0.129
3 2 1 4 3 2	1792.659	-0.080	0.318
		-0.079	0.347
3 2 2 4 3 1	1799.615	0.017	0.196
		0.016	0.199

In the first column of Table II we give the quantum numbers corresponding to the transition, in the second column – the frequency (cm^{-1}), next columns give the shift and the halfwidth of the line, ($\text{cm}^{-1}\cdot\text{atm}^{-1}$), in addition, the upper value denotes the measurement while the lower – the calculated result.

It can be noted that the calculated values of the line half-widths agree well with experiment: the deviation does not exceed 15% for 80% of all lines and the maximum deviation is 30% for the line centered at 1564.876 cm^{-1} . The standard deviation for the half-width is $0.052 \text{ cm}^{-1}\cdot\text{atm}^{-1}$.

Note that such an excess of the calculated results over the experiments can be explained by an ordinary disadvantage of the ATCF theory, namely, by the fact that the use of the perturbation theory for calculating the matrix elements of the scattering operator results in an overestimation of the calculated result by 10–13% (see Ref. 12).

The calculated shift values agree quite fairly well with the experiment. The correct shift sign has been obtained for all the lines and the deviation of the result of calculation from the experiment does not exceed $0.023 \text{ cm}^{-1}\cdot\text{atm}^{-1}$, which is comparable with measurement accuracy of Ref. 6. The linear deviations for the shift are less than 15% for 65% of all the lines and the standard deviation is $0.013 \text{ cm}^{-1}\cdot\text{atm}^{-1}$.

The numerical analysis performed has shown that the contribution of the first-order term $S_1(b)$ to the shift in the mixture $\text{H}_2\text{O}-\text{SO}_2$ in general is not large (it does not exceed 9%) and the principal interaction which forms the line center shift is the dipole-dipole interaction. In this case, a strong dependence of the shift on the rotational quantum numbers is observed up to the change of its sign and its value by an order

of magnitude. Note, however, that when calculating in other spectrum ranges (e.g., in the visible) the role of the first-order term can increase significantly.

The results of our calculations show that the ATCF method describes adequately the shifts of the water vapor lines due to the pressure of polar molecules. Note that our calculation does not include any fitted parameters.

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