### Influence of the intramolecular resonances on the interference of water vapor spectral lines

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In this paper we analyze the interference between lines of the IR spectra of water vapor, as well as the relations between intramolecular resonances (such as Coriolis, Fermi, Darling–Dennison, and more complex resonances) and nonlinear pressure dependence of line shift. Calculated results on the broadening and shift coefficients, as well as the parameters of cross-relaxation in the H<sub>2</sub>O–air, H<sub>2</sub>O–N<sub>2</sub>, and H<sub>2</sub>O–O<sub>2</sub> mixtures at temperatures of 200 to 300 K, are given for two lines in the 0.8  $\mu$ m region (634  $\leftarrow$  541, 8v<sub>2</sub> band centered at 12414.2027 cm<sup>-1</sup> and 652  $\leftarrow$  541, 3v<sub>1</sub> + v<sub>2</sub> band centered at 12413.9720 cm<sup>-1</sup>).

#### Introduction

The collision-induced interference among spectral lines in rotational-vibrational (RV) spectra of molecular gases is a subject of numerous investigations (see, for example, Refs. 1-10). The interference should be taken into account when studying absorption, emission, or Raman spectra of dense gases, as well as the absorption in atmospheric windows and microwindows, in the spectral line wings. To study the effect of interference on the spectroscopic parameters of spectral lines is of undoubted interest when solving problems connected with laser sensing; in particular, the effect of interference should be studied for atmospheric gases H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, and others in mixtures with nitrogen and oxygen at temperatures of 200 to 300 K.

It should be noted that the spectra of water vapor near 0.8 µm are due to the transitions to highly excited rotational-vibrational states, for which the intramolecular resonances are rather significant. In particular, for the two transitions considered in this paper, the resonance mixing makes up to 40%. In calculations, we used the technique from Refs. 8 and 9, which considers interference within the framework of the perturbation theory method. Matrix elements of the relaxation operator<sup>7</sup> were calculated in the impact approximation, and only the dipole-quadrupole interaction making the largest contribution was taken into account. In contrast to other papers devoted to estimates of the interference in the H<sub>2</sub>O molecule,<sup>5</sup> here we take into account the resonance mixing of wave functions of the upper states of the RV transitions.

The calculations showed that at a relatively low pressure effect of the interference on line shifts is weak for the overwhelming majority of the water vapor spectral lines. However, it may be significant for the lines, whose upper RV states are in strong resonance. Thus, there exists a relation between the intramolecular resonances of different types manifesting themselves due to anomalously strong rotational-vibrational interaction and the interference arising due to perturbation of molecular stationary states by collisions. The line interference leads to distortion of the Lorentzian profile of a line, nonlinear pressure dependence of the line shift, and to the increase of light absorption in the atmospheric transmission microwindows. The effect on atmospheric transmittance makes up to 3% for homogeneous near-ground paths.

### 1. Basic equations of theory of collisional broadening of interfering lines

In the collisional approximation, when the duration of a collision is short compared with the mean travel time, the absorption coefficient  $\alpha(\sigma)$  of a molecular gas having the partial density  $n_{\rm a}$  at the frequency  $\sigma$  can be presented as<sup>8</sup>

$$\alpha(\sigma) = (8\pi^2 \sigma) / (3\hbar c) n_a \text{ Im } I(\sigma);$$
  

$$I(\sigma) \sim \text{Tr } [d (\hat{\sigma} - \hat{L}_s - \hat{W})^{-1} d\rho^s]; \qquad (1)$$
  

$$\hat{W} \sim \langle \text{Tr } [(1 - U \otimes U^+) \rho^b \rangle.$$

Here d and  $\rho^{\rm s}$  are the dipole moment operator and the statistical operator of an absorbing molecule;  $\hat{\sigma}$ ,  $\hat{L}_{\rm s}$ , and  $\hat{W}$  are, respectively, Liouvillians of frequency and free molecule and the relaxation operator; the brackets denote averaging over states of a thermostat (density matrix  $\rho^{\rm b}$ ) and collisions; U is the two-particle scattering matrix; the product  $U \otimes U^{+}$  is understood in the Liouville meaning. To assess the absorption coefficient, we have to determine the scattering matrix, find the inverse matrix of the relaxation operator, and calculate the spur.

It is well known that in the case that the offdiagonal elements of the relaxation superoperator can be neglected, the matrix can be inverted trivially, and the absorption coefficient can be presented as a sum of contributions from individual lines having a dispersion line shape. If the off-diagonal elements of the relaxation superoperator are comparable with the diagonal ones, the line interference arises, namely, mutual effect of absorption at individual transitions, which can be interpreted as a "transfer" of absorption from one transition to another.<sup>12</sup> The interference may lead to strong distortions of the dispersion line shape, variation of the broadening coefficients, and to nonlinear pressure dependence of the line shift.

Hereinafter in this paper, we consider the case of weak interference, when the off-diagonal elements of the relaxation operator are much less than the diagonal ones in absolute value. In this case, to obtain the inverse operator in Eq. (1), we can use the perturbation theory and series expansion. The spectral function  $I(\sigma)$  in this case can be presented as a sum of contributions coming from individual lines numbered by the index k (quantum numbers of the initial and final states and transition are denoted as  $i_k \rightarrow f_k$ ), which can be presented as<sup>8,9</sup>

$$\operatorname{Im} I_{k}(\sigma) = \rho_{k} d_{k}^{2} \times \frac{P_{\mathrm{b}} \gamma_{k} + (\sigma - \sigma_{k} - P_{\mathrm{b}} \delta_{k} - P_{\mathrm{b}}^{2} \operatorname{Re}\Delta_{k}) (P_{\mathrm{b}} Y_{k})}{(\sigma - \sigma_{k} - P_{\mathrm{b}} \delta_{k} - P_{\mathrm{b}}^{2} \operatorname{Re}\Delta_{k})^{2} + (P_{\mathrm{b}} \gamma_{k})^{2}}, (2)$$

where  $P_{\rm b}$  is the buffer gas pressure (a binary mixture is considered),  $\gamma_k$  and  $\delta_k$  are the broadening and shift coefficients;

$$W_{kk} = iP_{\rm b} \gamma_k - P_{\rm b} \delta_k;$$
  

$$Y_k = 2 \sum_{k \neq l} \frac{d_l}{d_k} \frac{\text{Re } W_{lk}}{\sigma_l - \sigma_k};$$
(3)

$$\operatorname{Re}\Delta_{k} = 2 \sum_{l \neq k} \frac{\operatorname{Re} W_{kl} \operatorname{Re} W_{lk}}{\sigma_{l} - \sigma_{k}}.$$
 (4)

In Eqs. (2) and (3),  $\rho_k$  and  $d_k$  are the population of the lower level of a transition corresponding to the line with the number k and the matrix element of the dipole moment operator ( $\langle i_k | d | f_k \rangle$ );  $\sigma_k$  is the position of a line in vacuum;  $W_{kl}$  is the matrix element  $\langle i_k i_l | W | f_k f_k \rangle$  of the relaxation operator, which relates the lines with the numbers k and l.

As an example, Fig. 1 shows the line contour (2) for an individual line. This profile includes Lorentzian and dispersion terms and is asymmetric. As can be found from Eq. (2), the observed shift of the peak of the absorption coefficient  $\Delta \sigma_k^{exp}$  for an individual line is determined by the equation from Ref. 8:

$$\Delta \sigma_k^{\exp} = P_{\rm b} \delta_k + P_{\rm b}^2 \left[ (1/2) \gamma_k Y_k + \text{Re} \Delta_k \right] + O(P_{\rm b}^3).$$
(5)

In the general case, the equation for a line contour includes also the terms determining the squared pressure dependence of the line halfwidth. However, as was shown in Ref. 8, these terms are small and, therefore, neglected in Eq. (2). In the presence of interference, the line shift coefficient has a quadratic dependence on the buffer gas pressure, and a nonlinear dependence is determined by the off-diagonal matrix elements of the relaxation operator.



Fig. 1. Asymmetric contour of a line, Eq. (2), including the Lorentzian and dispersion terms.

The matrix elements  $W_{kl}$  were calculated by the perturbation theory,<sup>8,9</sup> and for short impact distances b the interruption approximation was applied,<sup>11</sup> according to which the matrix of the relaxation operator at  $b < b_0$  (interruption radius of the Anderson – Tsao – Curnutte theory<sup>11</sup>) becomes diagonal. Then

$$\gamma_{k} + i\delta_{k} = \frac{n}{c} \sum_{2} \rho(2) \int_{0}^{\infty} dvv F(v) \times \left[ b_{0}^{2}/2 + \int_{b_{0}}^{\infty} dbbS(b) \right];$$
(6)

$$W_{kl} = \frac{n}{c} \sum_{2} \rho(2) \int_{0}^{\infty} dvv F(v) \int_{b_{0}}^{\infty} dbb\Theta(b); \quad (7)$$
  
$$S(b) = S_{1}(b) + S_{2}(b) + \dots,$$

$$\Theta(b) = \Theta_1(b) + \Theta_2(b) + \dots$$
(8)

In Eqs. (6)–(8) quantum numbers are omitted for simplicity; F(v) is the Maxwell distribution function, the index 2 denotes the states of the buffer molecule and  $\rho(2)$  is the population of the level 2;  $S_1(b)$  and  $S_2(b)$  are the interruption functions of the Anderson–Tsao–Curnutte (ATC) theory. For the case of H<sub>2</sub>O lines broadening by nitrogen and oxygen, they have the following form:

$$S_{1}(b) = \frac{3\pi\alpha_{2}}{8\hbar\nu b^{5}} \bigg[ (\mu_{i}^{2} - \mu_{f}^{2}) + \frac{3}{2} \frac{I_{1}I_{2}}{I_{1} + I_{2}} (\alpha_{i} - \alpha_{f}) \bigg];$$
  
$$S_{2}(b) = \frac{1}{25\hbar\nu^{2} b^{2(l_{1}+l_{2})}} \times$$
(9)

$$\times \sum_{2'} Q^2(22') \left[ \sum_{i'} D^2(ii'_1) f(k_{ii'22'}) + (i \to f) \right],$$

where  $\mu_i^2$ ,  $\mu_f^2$ ,  $\alpha_i$ , and  $\alpha_f$  are the mean squares of the dipole moment and polarizability in the vibrational states *i* and *f*;  $I_1$  and  $I_2$  are ionization potentials;  $\alpha_2$  is polarizability of the buffer-gas molecule;  $Q^2(22')$  are the strengths of quadrupole transitions in N<sub>2</sub> (or O<sub>2</sub>);  $\Theta_1(b)$  and  $\Theta_2(b)$  are similar interruption functions for the off-diagonal elements of the superoperator *W* (Ref. 7):

$$\Theta_{2}(b) = \frac{1}{25\hbar^{2}\nu^{2} b^{6}} \sum_{2'} Q^{2}(22') \times \\ \times \left[ \sum_{i} D(ii') D^{*}(ii'') \varphi(k_{ii'22'}, k_{ii''22'}) \delta_{ff'} \delta_{j_{i}'j_{i}} + (10) \right. \\ \left. + \sum_{f} D(ff') D^{*}(ff'') \varphi(k_{ff'22'}, k_{ff''22'}) \delta_{ii'} \delta_{j_{f}j_{f''}} \right];$$

D(ii'|l) are the reduced matrix elements of the H<sub>2</sub>O dipole moment. In Eqs. (9) and (10)  $f_{l_1l_2}(k)$  and  $\varphi_{l_1l_2}(k, k')$  denote the so-called resonance functions; the resonance parameters

$$k_{ii'22'} = (2\pi cb) / \nu (\omega_{ii'} + \omega_{22'})$$
(11)

depend on frequencies of the virtual transitions in the absorbing and buffer-gas molecules.

## 2. Collisional interference in the IR spectra of water vapor

Earlier numerical estimates of the interference in water vapor<sup>5</sup> showed that the effect of interference on line broadening is very weak and can be neglected, at least, for lines of the rotational spectrum. The weakness of the interference effect is caused by the fact that  $H_2O$  molecule is a light asymmetric top with low moments of inertia and, consequently, large separations between the rotational energy levels. As a result, the transition frequencies  $\omega_{ff}$  and  $\omega_{ff}$  in Eq. (10) differ strongly, and the resonance functions

$$\varphi_{l_1 l_2}(k_{ff'22'}, k_{ff''22'}) \tag{12}$$

and the off-diagonal matrix elements of the relaxation operator prove to be small.

However, analysis in Ref. 5 has been performed for lines of the rotational spectrum of  $H_2O$ , and its results cannot be applied to transitions to excited vibrational states. Actually, for the transitions in the IR region and, especially, in the near infrared or visible regions, the rotational energy spectrum becomes denser. Besides, the vibrational dependence of molecular constants, i.e., rotational and centrifugal parameters of dipole moment, etc., as well as accidental Coriolis, Fermi, and Darling-Dennison resonances arising between close rotational energy sublevels of different vibrational levels, may turn out to be rather significant factors. As known, the first-order interruption function  $S_1(b)$  is purely imaginary and is determined by the isotropic part of the intermolecular potential.<sup>13</sup> This part of the function S(b) describes the main contribution to the shift of H<sub>2</sub>O lines in the near-IR and visible regions.<sup>13</sup> The anisotropic part of the intermolecular interaction (dipole–quadrupole potential in the case of H<sub>2</sub>O–N<sub>2</sub> or H<sub>2</sub>O–O) determines line broadening and only insignificantly contributes to the shift of rotational lines.

The off-diagonal matrix elements of the relaxation operator are determined, as a rule, by the anisotropic potential, the isotropic part of the intermolecular interaction and the term  $\Theta_1(b)$  in some cases cause the interference of vibrational bands,<sup>12</sup> but in the general case they contribute insignificantly to the interference between some water vapor RV lines. Therefore, we perform our further analysis for the case that the term  $\Theta_2(b)$  and the dipole-quadrupole interaction are the basic ones, but in calculation of the line shifts, we take into account the isotropic part of the induction and dispersion potentials.

According to Eq. (10), the quantum numbers of interfering lines in the second order of the perturbation theory must obey certain selection rules. Namely, the upper states of the corresponding transitions must have the same quantum numbers j, the rest quantum numbers [vibrational, which are denoted as V in aggregate  $(v_1, v_2, v_3 \text{ for H}_2\text{O})$ , and rotational denoted as  $R \ (\equiv K_a, K_c)$ ] may be different. Interference can be observed for transitions from the same lower state.<sup>\*</sup> Figure 2 shows the corresponding scheme of transitions and interactions. Analysis of Eqs. (10) and (11) yields the following conditions:

A) Since the upper states must be linked by the dipole transitions to a common "intermediate" state, they must have the same symmetry, and  $J_{f'} = J_{f''}$ .

B) It follows from Eqs. (10) and (11) that the upper states must have close energies, since the resonance functions  $\varphi_{l_1l_2}(k, k')$  decrease quickly as the difference |k - k'| increases. Consequently, the frequencies  $\omega_{ff'22'}$  and  $\omega_{ff''22'}$  must be close and the difference  $\Delta E = E_{f'} - E_{f'}$  must be small.

C) The reduced matrix elements of the dipole moment  $D(ff'|l_1)$  and  $D^*(ff''|l_1)$  corresponding to transitions from the common "intermediate" level f to the interfering levels f' and f'' must be rather large to give rise to interference. Therefore, the wave functions  $\Psi_{f'}$  and  $\Psi_{f''}$  and the dipole moment must have a large overlap area. In light multiatom molecules, such as

 $<sup>^{*}</sup>$  The effects of interference associated with the ground vibrational state can be neglected in the case of H<sub>2</sub>O, therefore only the second term should be kept in braces in Eq. (10).

 $H_2O$ , having high vibrational frequencies and large rotational constants, such overlapping of close levels of the same symmetry is possible only if they, first, belong to different vibrational states and, second, are coupled via some accidental resonance with the high degree of mixing of the wave functions. The wave functions of two resonating states can be presented as

$$\psi_1 = c\phi_1 + s\phi_2,$$
  

$$\psi_2 = -s\phi_1 + c\phi_2;$$
 (13)  

$$c = \cos(\beta), \ \beta = \arctan 2H_{12}/(H_{11} - H_{22}).$$

Here  $H_{11}$ ,  $H_{22}$ , and  $H_{12}$  are the matrix elements of the molecular Hamiltonian calculated with the wave functions  $\varphi_m$  of the nonresonance approximation. Then calculating the reduced matrix elements with the wave functions (13) and their product in the second term in braces in Eq. (10), we can demonstrate that

$$D(ff'|1) D^*(ff''|1) = -sc \ \mu_e^2 |\langle \varphi_1 | K_{xx} | \varphi_1 \rangle|^2.$$
(14)

In the case of an exact resonance  $s = c = \sqrt{2}/2$ .



**Fig. 2.** The scheme of rotational energy levels for two lines: [6 5 2 5 4 1] (310) and [6 3 4 5 4 1] (080). The rotational levels [6 5 2] (310) and [6 3 4] (080) are coupled by HEL (Highly Exited Local) resonance.

Thus, the matrix elements corresponding to the transitions shown in Fig. 2 are rather large and proportional to the constant dipole moment  $\mu_e = -1.8$  D. For other transitions that couple nonresonance levels, the matrix elements are proportional to derivatives of the dipole moment with respect to internal coordinates and those are at least an order of magnitude smaller (the largest dipole moment

derivative for  $H_2O$  is 0.16 D). Consequently, the interference must manifest itself for lines involved in accidental resonances – all the three conditions above are fulfilled in this case.

# 2.2. Calculating the broadening and shift coefficients, as well as cross-relaxation parameters for $H_2O-N_2$ and $H_2O-O_2$

The test calculations showed that for nonresonating lines of a vibrational band the effect of interference is weak and gives rise to a weak nonlinearity – the coefficients  $Y_k^0$  have the values of the order of  $10^{-4}$ , being in close agreement with the data from Ref. 5.

The coefficients  $Y_k^0$  of the nonlinear pressure dependence of the line shift, as well as the parameters  $W_{kl}$ , halfwidths, and shift coefficients were calculated for two lines  $[652](310) \leftarrow [541](000)$  and  $[634](080) \leftarrow [541](000)$  of H<sub>2</sub>O in the region of 0.8 µm in the cases of broadening by nitrogen and oxygen under the pressure up to 10 atm. The relaxation parameters of lines in air were determined by the equation:

$$X(air) = 0.79 X(N_2) + 0.21 X(O_2),$$
 (15)

where X is any of the parameters  $\gamma_k$ ,  $\delta_k$ ,  $Y_k^0$ , or  $W_{kl}$ . The rotational levels of the vibrational state (080) were borrowed from the Partridge and Schwenke calculation.<sup>15</sup> For the vibrational state (310) they were calculated through diagonalization of the effective rotational Hamiltonian matrix. The wave functions needed for in calculation were also determined as eigenfunctions of the effective rotational Hamiltonian in the nonresonance approximation. The mixing coefficient ( $s^2$ , see Eq. (14)) was determined from the observed line intensities.<sup>14</sup> The polarizabilities  $\alpha_{080}$  and  $\alpha_{310}$  were calculated by the equation

$$\alpha_{v_1v_2v_3} = \alpha_{000} + \alpha_1v_1 + \alpha_1v_2 + \alpha_1v_3, \quad (16)$$

the coefficients  $\alpha_i$  determining the vibrational dependence were borrowed from Ref. 13. The rest parameters used in calculations are given in Table 1. The calculated results are shown in Fig. 3 and presented in Table 2.

Table 1. Molecular parameters used in calculations

Parameter	$H_2O$	N <sub>2</sub>	O <sub>2</sub>
Rotational and centrifugal constants, in cm <sup>-1</sup>	From Ref. 16	$B_0 - 1.998,$ $D_0 - 5.76 \cdot 10^{-6}$	
Dipole moment, in D	1.859	0	0
Quadrupole moment, in D·Å Polarizability,	2.9	3.0	0.8
in Å <sup>3</sup> Ionization	14.69	17.6	16.1
potential, erg	2.018	2.485	2.003

the band $3v_1 + v_2$ (centered at 12413.9720 cm <sup>-1</sup> ) at broadening by N <sub>2</sub> , O <sub>2</sub> , and air										
Buffer-gas	Parameter	Temperature, K								
molecule		200	230	260	297	330	n			
Line 634←541 (080)										
$N_2$	$W_{kl}$	-4.6	-4.0	-3.5	-3.1	-2.8	0.97			
	$Y_k$	41	35	31	27	24	1.01			
	$\gamma_k$	79	75	71	67	63	0.47			
	$\delta_k$	-49	-40	-34	-28	-24	1.43			
$O_2$	$W_{kl}$	-3.6	-3.0	-2.6	-2.3	-2.0	1.11			
	$Y_k$	31	26	23	20	17	1.17			
	$\gamma_k$	34	32	30	28	27	0.47			
	$\delta_k$	-73	-63	-55	-48	-43	1.05			
Air	$Y_k$	38	33	29	25	22	1.04			
	$\gamma_k$	69	66	62	59	55	0.47			
	$\delta_k$	-54	-45	-38	-32	-28	1.30			
Line 652 (310)										
$N_2$	$\gamma_k$	87	81	78	73	70	0.44			
	$\delta_k$	-26	-21	-17	-14	-12	1.52			
$O_2$	$\gamma_k$	37	34	33	31	30	0.39			
	$\delta_k$	-47	-40	-35	-30	-27	1.10			
Air	$\gamma_k$	76	71	68	64	62	0.40			
	$\delta_k$	-30	-25	-21	-17	-15	1.43			

Table 2. Halfwidth  $\gamma_k$ , shift coefficients  $\delta_k$ , off-diagonal matrix elements  $W_{kl}$ , coefficients of the quadratic dependence  $Y_k$  (10<sup>-3</sup> cm<sup>-1</sup>/atm), exponents of temperature dependence n for the lines 634  $\leftarrow$  541 of the band 8v<sub>2</sub> (centered at 12414.2027 cm<sup>-1</sup>) and 652  $\leftarrow$  541 of the band 3v<sub>1</sub> + v<sub>2</sub> (centered at 12413.9720 cm<sup>-1</sup>) at broadening by N<sub>2</sub>, O<sub>2</sub>, and air

Note: For the line  $652 \leftarrow 541$  (310) the parameters  $W_{kl}$  are the same as for the line  $634 \leftarrow 541$  (080), while the parameters  $Y_k$  have opposite signs.



**Fig. 3.** Pressure dependence of shift of the line [6 5 2 5 4 1] (310) (nonlinear shift is calculated by Eq. (5)).

For the above-mentioned lines involved in the HEL resonance<sup>14</sup> caused by anomalously strong centrifugal effect in  $H_2O$ , we observe the strong effect of interference – the coefficients  $Y_k^0$  have the values about 0.02 cm<sup>-1</sup>/atm at the room temperature. For the upper states of the considered transitions, the mixing coefficient of wave functions is  $s^2 = 0.4$ , the line positions differ only by 1 cm<sup>-1</sup>, and this leads to a large value of the relaxation parameter. Figure 3 shows the dependence of the line shift on the nitrogen pressure – it is markedly nonlinear. At a pressure about 3 atm, the correction caused by the second term in Eq. (5) is 0.03 cm<sup>-1</sup>, and thus it can be easily measured with ordinary spectroscopic devices.

### 3. Temperature dependence of the cross-relaxation parameters

To calculate the atmospheric transmittance, one should take into account the temperature dependence of the line shape parameters: halfwidth and line shift, as well as determine the temperature dependence of the off-diagonal matrix elements of the relaxation operator. For this purpose, we have calculated the parameters  $W_{kl}$ ,  $Y_k$ , halfwidths, and shifts in the temperature range of 200 to 330 K.

The exponents of the temperature dependence n were determined by the least squares method using the equation

$$X(T) = X(297) (297/T)^{-n},$$
(17)

where X is any of the parameters  $W_{kl}$ ,  $Y_k$ ,  $\gamma_k$ , or  $\delta_k$ . These values are given in Table 2. Note that the cross-relaxation parameters increase rather strongly as the temperature decreases.

### 4. Effect of interference of water vapor spectral lines on atmospheric transmittance for the near-IR radiation

To estimate the effect of interference on the atmospheric absorption function, we have performed calculations in the region of  $12412-12415 \text{ cm}^{-1}$ , the two lines with the centers at  $12414.2027 \text{ cm}^{-1}$  and  $12413.9720 \text{ cm}^{-1}$  fall in.

These lines are due to the transitions  $634 \leftarrow 541$  of the band  $8\nu_2$  and  $652 \leftarrow 541$  of the band  $3\nu_1 + \nu_2$  that are considered here. Two series of calculations have been performed. In the first one, the line interference was ignored and the Lorentzian profile was used. In the second one, the profile (2) was applied that accounts for the interference.

The needed parameters were taken from Table 2, and the line intensities were borrowed from Ref. 14. The calculations were made for a horizontally homogeneous near-ground path 100–1000 m long. At the temperature of 297 K and air pressure of 760 Torr only water vapor absorption was taken into account.

Figure 4a shows the spectrum of atmospheric absorption, and Fig. 4b shows the difference between the absorption calculated by use of the Lorentzian profile and that calculated with the allowance made for the interference.



**Fig. 4.** Calculated atmospheric absorption A near 12414 cm<sup>-1</sup>. Path length of 400 m. Dots are for the absorption calculated with the allowance made for interference (*a*) and the relative contribution (%) of H<sub>2</sub>O line interference to the atmospheric absorption of radiation at v = 12414 cm<sup>-1</sup> (*b*).

The calculations showed that the effect of interference is weak – the largest addition is about only 3% as small at the wavenumber of  $12414.07 \text{ cm}^{-1}$  between the lines, the line interference leads to the increase of absorption in atmospheric transmission microwindows.

### 5. Discussion and conclusions

The results obtained in this work suggest the following conclusions.

1. Line interference and intramolecular resonances in the  $\rm H_2O$  molecule turn out to be related, namely: stationary RV states of molecules, in which there is a strong difference from the "rigid rotator – harmonic oscillator" model and different vibrational modes prove to be mixed, are mixed further by collisions. This leads to deviation of the line shape from the Lorentzian shape and the marked nonlinear pressure dependence of the line position already at low pressure. It should be emphasized that the line position (line center) here is the experimentally observed peak of the absorption coefficient.

2. In this work, we took into account only the long-range dipole-quadrupole interaction; calculations were performed for pressures up to 10 atm. For the  $H_2O-N_2$  system, the dipole-quadrupole approximation is valid for lines with low values of the angular momentum quantum number; corrections associated with the short-range forces may be significant for lines with high J. Expansion of the short-range potential into a series over inverse powers of the intermolecular distance leads to the appearance of additional terms of various tensor character. As a consequence, the selection rules for interfering lines given above in Conditions A and B may be complemented with new ones. If the studied gas is at a high pressure, about tens atmospheres, the line overlapping leads to a significant interference of almost all lines.

3. The effect of interference of water vapor spectral lines on the atmospheric transmittance in the near-IR region for the transitions considered in this paper is several percent in the region of  $0.8\,\mu\text{m}.$  Obviously, corrections for the line interference should be taken into account in analysis of high-resolution atmospheric spectra.

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