H_2O ABSORPTION LINE SHIFTS IN THE $\nu_1 + 3\nu_3$ BAND INDUCED BY NOBLE GAS PRESSURE

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Results of measurements of the H_2O *line shift coefficients in the* $\nu\nu_1 + 3\nu\nu_3$ *absorption band induced by noble gas atoms* (He, Ne, Ar, Kr, *and* Xe) *are presented. Simple relationships connecting the shift value with perturbing atom polarizability have been obtained. Experimental results and problems of further development of the theory are discussed.*

INTRODUCTION

Experimental and theoretical investigations of molecular spectral line shifts induced by collisions with atoms or molecules are important for understanding of the nature of intermolecular forces. They yield information about characteristics of intermolecular interaction potential, collision cross section, and molecular polarizability in excited states.[1] There is a justified assumption that line shift coefficients are more sensitive to variation of intermolecular interaction potential characteristics than half–widths. Investigation of absorption line shifts of H_2O, O_3, CO_2, and CH_4 molecules in the infrared and visible regions are also of practical interest, since these gases determine extinction in planetary atmospheres. The accurate H_2O line shift coefficients are necessary for solving the inverse problem of sounding of water vapor concentration along vertical and slant paths.[2] Data on broadening and shift of spectral lines by He and H_2 gases can be used for analysis of light–induced drift in stellar atmospheres.

Problem of molecular spectral line shifting by inert gas pressure is of special interest in collision theory. This case is the simplest one since noble gas atoms have closed electron shells and have no permanent electric moments in the ground electron state. Energy required to excite inert gas atom is larger than mean thermal energy, and inert gas atoms can be considered as structureless particles. For this reason a set of experimental data on shifts δ and half–widths γ of absorption lines induced by inert gas pressure and measurements of δ and γ dependence on atomic mass or atom polarizability are extremely important for check of different methods commonly used for calculation of these values, in particular, methods using direct calculation of scattering matrix elements,[3] for accuracy.

The current state of the art of investigations in the shifts of the H_2O spectral lines caused by atomic gas pressure is as follows. The dependence of shift coefficient to broadening coefficient ratio on collision duration for water vapor absorption lines corresponding to the $7_{07} - 8_{18}$ transition of the ν_2 band measured using a diode laser spectrometer is presented in Ref. 4. Its analysis points to a distinction between formation of line shifts due to pressure of light (He and Ne) and heavy (Xe) particles, for nonadiabatic processes are prevailing in the former case, and adiabatic ones – in the latter. Measurements of water vapor absorption line shifts due to Ar and Xe pressure in the IR and visible ranges are presented in Refs. 9 and 24. Data on shift and half–width dependence on polarizability of buffer inert gas atoms for one of the absorption lines of the $\nu_1 + 3\nu_3$ band are given in Ref. 5, although without thorough analysis and comparison with theoretical calculation data.

In calculating shifts and half–widths of molecular spectral lines by the semiclassical collision theory, the following circumstances are substantial.

First, in a number of cases even the simple theory (Anderson–Tsao–Curnutte (ATC) approximation[6]) is able to give rather accurate values of line shift coefficients. That is valid in the case of line broadening due to collisions with polar molecules. In particular, even such a phenomenon as oscillating shifts, i.e. alternation of a shift sign as a function of parity of the quantum number J for one vibration band of HCl molecule, is well described by the ATC method.[7] Satisfactory agreement between calculated and experimental values is obtained for NH_3, H_2O, and some other molecules for self–broadening or broadening by collisions with polar molecules.[8–11]

Comparison of calculated and experimental values of shifts induced by collisions with nonpolar molecules shows that a certain modification of the ATC method with adjustable parameters (polarizability of molecule in upper vibrational state) allows one to reach agreement with experimental data on H_2O lines broadened due to collisions with H_2O, N_2, and O_2 molecules in the near–IR and visible regions. At the same time there is disagreement with data for water vapor absorption bands obtained with Fourier spectrometers.

The reason for such disagreement has not yet been understood: it could be as measurement errors as disadvantages of theoretical models. However, to calculate the H_2O spectral line shift coefficients by the pressure of some buffer gases, for instance, H_2 (see Ref. 12) or inert gases[5] or to calculate the shift coefficients for O_3 line broadened by collisions with N_2 or O_2 (see Ref. 13), calculation methods, in any case, should be modified abandoning some simplifications, such as straight trajectory approximation, interruption procedure, and isolated line approximation.

Nevertheless, unnecessary complexity of calculations is undesirable; simplicity and validity of the ATC method should be retained. Data on the dependences of molecular

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spectral line shifts and broadening induced by collisions with inert gas atoms are necessary for theoretical models to be refined, since they allow one to follow variation of the character of the interaction of colliding particles attendant to disturbing atom mass or polarizability variation.

Second, when calculating shift coefficients, account must be taken of vibrational dependence of intermolecular potential, in particular, of its isotropic part. At collisions with inert gas atoms, line shift is determined by induction and dispersion interactions that contribute to the first and second orders of the interruption function.[19] As to the shift value, it is determined by polarizability of absorbing molecule in excited vibrational state and by polarizability of buffer gas atom. As shown in Ref. 1, there is the opportunity to determine the parameters of polarization interaction from shift value as well as to determine the vibrational dependence of polarizability. It seems likely that the dependence even of individual components of polarizability tensor of absorbing molecule in excited state[14] on vibrational quantum numbers may be determined from the shift value.

We consider that spectral line shift measurements furnish the real opportunity to estimate the dependence of the parameters of intermolecular interaction potential on the vibrational quantum number, especially in the case of interaction of molecules with inert gas atoms, when contribution of electrostatic interactions is absent. In addition to the above–mentioned opportunities to refine the method of shift calculation (abandonment of the perturbation theory and of the Anderson interruption procedure, account of trajectory bending of colliding particles, etc.), the Unsöld approximation[14] must be tested. This approximation is used to calculate induction and dispersion interaction energies and permits to express their values in terms of the polarizability and the first ionization potentials of absorbing molecule and buffer atom (molecule). If conditions of applicability of the Unsöld approximation are violated, the absorbing molecule polarizability cannot be estimated. If the Unsöld approximation is valid, the absorbing molecule polarizability in excited vibrational state can be determined for specific collision partner, and this polarizability value can be subsequently used for calculation of line shifts induced by pressure of other gases.

Third, when passing from pure rotational spectrum (microwave region) to vibration–rotation spectrum (transition into highly excited vibrational states, i.e., short wave region), measurable line shifts grow. Accuracy in determining the polarizability from the data on line shifts in the near–IR and visible regions is higher. Moreover, since in these spectral regions shift values (for H_2O absorption lines, for example) are determined by vibrational effect, just in these spectral regions shift data processing has much potential for yielding comprehensive and precise information about the dependence of the intermolecular interaction potential parameters on the vibrational quantum numbers.

Our study is aimed at measuring the line shift coefficients in the water vapor $\nu_1 + 3\nu_3$ band induced by collisions with inert gas atoms (He, Ne, Ar, Kr, and Xe), calculating the shift values, and comparing our experimental results with theoretical ones and with experimental results obtained elsewhere.

EXPERIMENT

Measurements of line shifts of the water vapor $\nu_1 + 3\nu_3$ absorption band induced by pressure of He, Ne, Ar, Kr, and Xe were carried out using a two–channel opto–acoustic spectrometer with tunable ruby laser. Specifications of the spectrometer were the following:

– spectral resolution	no worse than 0.013±±0.002 cm;
–absorption coefficient limiting sensitivity	$5{\cdot}{\cdot}10^{-8}$ cm^{-1};
– laser frequency tuning range	14397–14405 cm^{-1}.

Two opto–acoustic cells were placed one after the other along the laser beam axis. Both cells were connected with a vacuum system intended to pump a gas or gas mixture at a given pressure into the cells and to bleed the cells. Usually, the first cell was filled with pure water vapor at a pressure of several Torr, while the second cell was filled with the same amount of water vapor mixed with buffer gas.

Thus, in experiment both Doppler shape of water vapor absorption line centered at unshifted frequency (the first cell) and shape of the same line broadened and shifted by collisions with atoms or molecules of buffer gas (the second cell) were simultaneously recorded. The lasing wavelength was changed discretely from pulse to pulse. Spectral width as well as changes in the laser radiation wavelength were measured by the Fabry–Perot interferometer with a spectral resolution of no worse than 0.002 cm^{-1}. Interference pattern and interference fringe diameters that were used to calculate the wavelength change were recorded by a photoelectric registration system.

Shift value was determined from the shift of the maximum in the absorption line profile of H_2O mixed with inert gas (the second opto–acoustic cell) from the maximum in the pure H_2O absorption line Doppler profile at low pressure (the first cell). Shift measurements were performed at fixed pressure varying from 100 to 760 Torr. In processing of the profiles measured for discrete wavelength change the algorithm of experimental point fitting to the Voigt profile, proposed in Ref. 15, was used. As it was tested, in shift measurement within the limits of experimental error, which according to Ref. 5 was equal to 0.002 cm^{-1}, shift of H_2O spectral line under study for each of inert gases depended linearly on buffer gas pressure. After that the value of shift coefficient was determined. Experimental shift coefficients are listed in Table I (the second column).

In Table II, comparison of measurement errors for H_2O absorption line shifts and half–widths obtained using different laser spectrometers in the visible and IR is presented. Table II illustrates the possibilities of the two–channel opto–acoustic spectroscopy method using small cells as compared with multichannel Bouguer cells, to investigate shifts of very weak spectral lines (absorption in maximum is $\le 10^{-7}$ cm^{-1}). Accuracy of measurements, even for pulsed laser, is quite high. In addition to measurements of the H_2O absorption line shifts, experimental data on their half–widths are listed in Table I (last column).

The dependence of shift and broadening coefficients on buffer gas atom polarizability measured with a two–channel opto–acoustic spectrometer is shown in Fig. 1. The data from Ref. 9 obtained using a laser spectrometer for H_2O absorption line belonging to the $\nu_1 + 3\nu_3$ band, i.e. the band examined by us, are also plotted in Fig. 1.

TABLE I. Experimental and calculated coefficients of water vapor line shifts due to pressure of noble gases for the 4_{14}–5_{15} *transition of the* $\nu_1 + 3\nu_3$ *band.*

Buffer gas	Line shifts coefficient, $cm^{-1} \cdot atm^{-1}$				Half–width, $cm^{-1} \cdot atm^{-1}$
	Experiment	δ_1	δ_{11}	δ_3	Experiment
He	0 ± 0.002	–0.022	–0.011	–0.006	0.024 ± 0.006
Ne	–0.005 ± 0.002	–0.021	–0.017	–0.010	0.027 ± 0.006
Ar	–0.035 ± 0.002	–0.31	–0.032	–0.032	0.053 ± 0.006
Kr	0.043 ± 0.002	–0.034	–0.039	–0.039	0.075 ± 0.006
Xe	–0.043 ± 0.002	–0.039	–0.053	–0.053	0.093 ± 0.006

TABLE II. Specifications of laser spectrometers for investigation of the H_2O *absorption line broadening and shifting by foreign gas pressure.*

Laser spectrometer type (spectral range, buffer gases)	Laser type, Lasing line width, cm^{-1}	Measuring error		Ref.
		Line center or line shift, cm^{-1}	Half–width, cm^{-1}	
Spectrophotometer with White cell 920–1070 cm^{-1}, (010), H_2O, N_2	Diode laser $2 \cdot 10^{-4}$	–	$4 \cdot 10^{-4}$	25
Spectrophotometer with multipass cell 1280–1300 cm^{-1}, (020), H_2O, O_2, N_2	Diode laser $3 \cdot 10^{-5}$	Shift $2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	24
Spectrophotometer with White cell 1946–1980 cm^{-1}, (020), H_2O, O_2, N_2	Diode laser $3 \cdot 10^{-5}$	Line center $1 \cdot 10^{-4}$ Shift $2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	26–28
IR spectrometer H_2O, N_2, CO_2, CO, CH_4, He, Ne, Ar, Kr, Xe	Diode laser 10^{-4}–10^{-5}	Line center, shift $(0.6–4) \cdot 10^{-4}$	$1 \cdot 10^{-4}$	4
Spectrophotometer with ring Nd–glass laser 9240–9520 cm^{-1}, (012), air	Nd–glass laser $7 \cdot 10^{-5}$	Shift $3 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	2
Spectrophotometer, 10350 cm^{-1}, (102), H_2O, N_2, air	–	Shift $2 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	29
Two–channel spectrophotometer with White cell (2 m), 13350–13950 cm^{-1}, (221, 202, 301, 141, 042, 320, 122), H_2O, O_2, N_2, Ar,Xe,air	Ring dye laser $1 \cdot 10^{-4}$	Line center, shift $1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	9, 21, and 22
Two–channel OA spectrometer 13700–14000 cm^{-1}, (301), air	Pulsed dye laser $1 \cdot 10^{-4}$	Line center $1 \cdot 10^{-3}$ Shift $2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	30
Spectrophotometer with White cell (30 m), 16100–17450 cm^{-1}, (401), H_2O, air	Ring dye laser $7 \cdot 10^{-4}$	Line center, $1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	31
Two–channel intracavity OA spectrometer, 16100–17450 cm^{-1}, (401), CH_3–CO–CH_3, air	Dye laser $1 \cdot 10^{-3}$	Line center, shift $1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	32

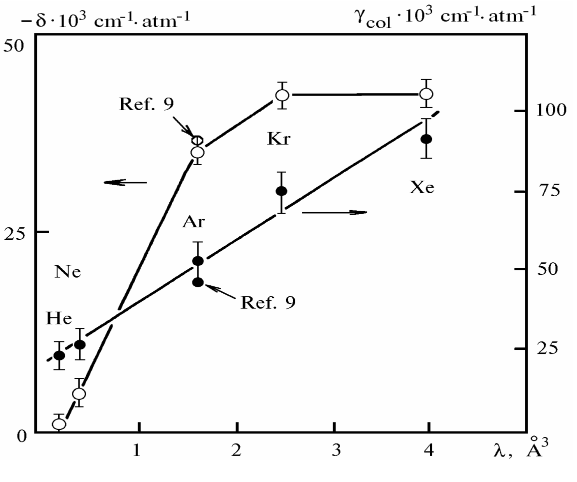

FIG. 1. Collision broadening coefficients (γ_{col}) *and shift coefficients* (δ) *of the* H_2O *absorption line* (ν_3 = 14397.3638 cm^{-1}) *as functions of the polarizability of buffer inert gases.*

SHIFT COEFFICIENT CALCULATIONS

The value of the H_2O molecule polarizability in the (103) vibrational state was borrowed from Ref. 1 where it was determined from the measured shifts of the same lines belonging to the $\nu_1 + 3\nu_3$ band due to air pressure. Therefore, calculations of the H_2O absorption line shift coefficients due to inert gas pressure can be considered as predictive.

Preliminary calculations by the ATC method taking into account polarization interaction for the first and second orders of interruption function as well as vibrational dependence of polarizability and dipole moment of the H_2O molecule have shown the following:

First, it is polarization interactions included in the first–order term of the interruption function $S(b)$ which makes the main contribution to the shift value (about 90%).

Second, shift coefficient dependence on the rotational quantum number is weak.

Third, interruption radius is very small and varies from 2Å for H_2O–He collisions to 4Å for H_2O–Xe case.

In accordance with the classification proposed in Ref. 16, collisions of H_2O molecule with light atoms should be considered as weak. In full resonance approximation, collisions of H_2O molecule with He and Ne (actually, in this case there is no resonance energy exchange since perturbing atom is considered as a structureless particle) the minimum impact parameter b_0 estimated by the ATC theory is smaller than the distance of closest approach r_0 (see Ref. 16). Results from Ref. 16 and our preliminary calculations show that the standard ATC method introduces significant error. For this reason, modification of the method is required.

The trajectory bending effect for H_2O molecule collisions with He and Ne atoms was estimated in Ref. 17. This effect makes a correction for the line shift value up to 45% and leads to its decrease.

To calculate the H_2O line shift coefficients due to inert gas pressure, let us apply the method proposed in Ref. 18, which eliminates the Anderson interruption procedure. In this case the expression for the line shift coefficient is written as

$$d = \frac{n}{c} \int\limits_0^\infty F(V)\, V\, \mathrm{d}V \times$$

$$\times \int\limits_0^\infty b\, \mathrm{d}b \exp[-\mathrm{Re}\, S_2(b)] \sin[(S_1(b) + \mathrm{Im}\, S_2(b)], \tag{1}$$

where n is the buffer gas particle concentration, c is the speed of light in vacuum, V is the relative velocity of colliding particles obeying the Maxwell velocity distribution function $F(V)$, and b is the impact parameter. Summation over the buffer particle rotational states is absent since the energy spectra of atom have no rotational structure. In this case the interruption function $S(b) = S_1(b) + S_2(b)$ is determined by contributions of polarization interaction

$$S_1(b) = \left(-i\frac{3\pi}{8 h V b^5}\right)\{(d^2_{\mathrm{v}_i} - d^2_{\mathrm{v}_f})\,\alpha_2 + \bar{\varepsilon}\,\alpha_2\,(\alpha_{\mathrm{v}_i} - \alpha_{\mathrm{v}_f})\}, \tag{2}$$

$$\mathrm{Re}\, S_2(b) = \frac{21\,\pi^2}{1280\,(h\,V)^2\, b^{10}} \left\{\sum_{i'} C_{20}\,(i2;\, i'2)\ \mathrm{Re}\ g_1(k_{i\,i'}) + \right.$$

$$\left. + \sum_{f'} C_{20}(f\,2; f\,'2)\,\mathrm{Re}\ g_1(k_{f\,f\,'}) - 2WC_{20}(i2;\, i2)\ C_{20}(f\,2;\, f\,2)\right\}$$
,(3)

$$\mathrm{Im} S_2(b) = \frac{21\,\pi^2}{1280\,(h\,V)^2\, b^{10}} \left\{\sum_{i'} C_{20}\,(i2;\, i'2)\ \mathrm{Im}\ g_1(k_{i\,i'} - \right.$$

$$\left. - \sum_{f\,'} C_{20}\,(f\,2;\, f\,'2)\ \mathrm{Im}\ g_1\,(k_{i\,i'})\right\}. \tag{4}$$

Here d_{v_i} and d_{v_f} are the dipole moments of H_2O molecule in the ground (i) and excited (f) vibrational states, respectively; α_{v_i} and α_{v_f} are the corresponding polarizabilities; α_2 is the polarizability of buffer atom; $\bar{\varepsilon} = \varepsilon_1\varepsilon_2/(\varepsilon_1 + \varepsilon_2)$; ε_1 and ε_2 are the ionization potentials of H_2O molecule and buffer atom, respectively; $C_{20}(i2;\, i'2)$ and $C_{20}(f2;\, f'2)$ denote squares of reduced matrix elements that determine probability of $i \to i'$ and $f \to f\,'$ transitions in H_2O molecule. Expressions for them are derived in Ref. 19, the indices "2" in $C_{20}(i2;\, i'2)$ and $C_{20}(f\,2;\, f\,'2)$ refer to the perturbing particle quantum numbers; $\mathrm{Re}\, g_1(k)$ and $\mathrm{Im}\, g_1(k)$ denote the real and imaginary parts of resonance function; $k_{ii} = 2\,\pi\, c\, b\, \omega_{ii}/V$ is the Massey parameter depending on virtual transition frequencies $\omega_{ii'}$, impact parameter b, and relative velocity V of colliding particles, and $\omega = j_i\, i_f\, j_i\, i_f|$ is the Racah coefficient.

Expressions (2)–(4) diverge as $b \to 0$, so that the integral over the impact parameter in Eq. (1) diverges at its lower limit in analogy with the case of the ATC theory, where this divergence is eliminated by using the interruption procedure.

If the dependence on the impact parameter in the exponent is reduced to a power–law function by way of using approximate expression for $\mathrm{Re}\, S_2(b)$ and the second factor of the integrand is expanded into a series, integral (1) can be analytically calculated. It allows one to calculate integral (1) without resorting to the interruption approximation, and exponential factor in the integrand becomes "truncation factor".

Calculation in Ref. 1 has shown that for lines in the visible spectral region $|S_1(b)| \gg |\mathrm{Im}\, S_2(b)|$ and $\mathrm{Im}\, S_2(b)$ can be ignored. Moreover, the third term in Eq. (3) is two orders of magnitude less than the sum of the first two terms and, consequently, it can be ignored too. For calculation we use mean velocity and full resonance approximations $k_{ii} = 0$; in this case $\mathrm{Re}\, g_1(k_{ii}) = 1$ and expression (3) for the real part of the interruption function is simplified.

Let us introduce the notation

$$A = \frac{21\,\pi^2}{1280\,(h\,V)^2} \left\{\sum_{i'} C_{20}(i2;\, i'2) + \sum_{f'} C_{20}(f\,2;\, f'\,2)\right\}, \tag{5}$$

$$B = \left(-\frac{3\,\pi}{8\,h\,V}\right)\left\{(d^{\,2}_{\mathrm{v}_i} - d^{\,2}_{\mathrm{v}_f})\alpha_2 + \frac{3}{2}\,\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}\,\alpha_2(\alpha_{\mathrm{v}} - \alpha_{\mathrm{v}_f})\right\}. \tag{6}$$

In the above–indicated approximations equation (1) can be represented in the following form:

$$\delta = \frac{n\,V}{2\,c} \int\limits_0^\infty b\ \mathrm{d}\ b\ \exp\left[-\frac{A}{b^{10}}\right]\frac{B}{b^5}\,. \tag{7}$$

Making the substitution of variable $Ab^{-1} \equiv x$, we obtain

$$\delta = \frac{n\,V}{2\,c}\,\frac{BA^{-3/10}}{10} \int\limits_0^\infty \mathrm{d}\ x\ e^{\,-x}\ x^{(-3/10\,-\,1)}\,. \tag{8}$$

The integral is reduced to tabular [20] and is expressed in terms of the Γ–function. We finally derive

$$\delta = \frac{n\,V}{2\,c}\,BA^{\,-0.3}\,(0.1)\,\Gamma\,(0.3). \tag{9}$$

Expression (9) is analogous to expression for line shift in the ATC method but instead of interruption parameter $b_0^{-3/2}$ of the Anderson theory[6] it contains $DA^{-3/10}\, G(0.3)$. Taking into account resonance conditions, line strengths $C_{20}(i2;\, i'2)$ and $C_{20}(f\,2;\, f\,'2)$ after summation over virtual transitions take the form

$$C_{20}\,(i2;\,i'2) = \frac{1-\sqrt{3/2}}{\sqrt{2}}\,d^{\,2}_{\nu_i}\,\alpha_2 + \frac{2}{\sqrt{2}}\,\bar{\varepsilon}\,\alpha_2\,(\alpha_{v_i} - \alpha_{z\,z}^{\,i}), \qquad (10)$$

$$C_{20}\,(f2;\,f'2) = \frac{1-\sqrt{3/2}}{\sqrt{2}}\,d^{2}_{f_i}\,\alpha_2 + \frac{2}{\sqrt{2}}\,\bar{\varepsilon}\,\alpha_2\,(\alpha_{\nu_f} - \alpha_{z\,z}^{\,f})\ .$$

Here $\alpha_{z\,z}^{\,i}$ and $\alpha_{z\,z}^{\,f}$ are z–components of H_2O polarizability tensor for i and f states, respectively. The value of $a_{z\,z}^{\,f}$ was estimated so that z–component variation was proportional to mean polarizability variation at H_2O molecule vibration excitation. Substituting Eq. (10) into Eq. (5), and Eqs. (5) and (6) into Eq. (9), we derive a simple expression for line shift coefficient in the impact approximation, which takes into consideration vibrational dependence of shifts and contributions from collisions with small impact parameters $b < r_c$

$$\delta = \frac{n}{2\,c}\,(0.1)\Gamma\,(0.3)\left(-\frac{3\,\pi}{8\,h}\right)\{(d^{\,2}_{\nu_i} - d^{\,2}_{\nu_f})\,\alpha_2 + \bar{\varepsilon}\,\alpha_2(\alpha_{\nu_i} - \alpha_{\nu_f})\}\times$$

$$\times\ \left\{\frac{21\pi^2}{1280(h\ V)^2}\left[\frac{1-\sqrt{3}}{\sqrt{2}}\,(d^{\,2}_{\nu_i} - d^{\,2}_{\nu_f})\alpha_2 + \right.\right.$$

$$\left.\left. + \frac{3}{\sqrt{2}}\,\bar{\varepsilon}\,\alpha_2(\alpha_{\nu_i} - \alpha_{z\,z}^{\,i} + \alpha_{\nu_f} + \alpha_{z\,z}^{\,f})\right]\right\}^{-0.3}. \qquad (11)$$

Analogous expressions for line broadening coefficients were obtained earlier.[23] Expression (11) is independent of the rotational quantum numbers. It depends only on vibrational quantum numbers, which is manifested in the vibrational dependence of polarizability tensor components.

DISCUSSION OF RESULTS

It should be noted that measurements reported in Refs. 4, 5, 9, and 21 demonstrate weak shift dependence on the rotational quantum numbers. For example, line shift coefficient in the $\nu_1 + 3\nu_3$ band due to Ar pressure varies from -0.0280 for $j = 0$, $K_a = 0$ to -0.0421 cm^{-1} atm^{-1} for $J = 9$, $K_a = 0$, i.e. by 50% (see Ref. 9). At the same time for broadening by N_2, line shift coefficients vary from 0.0070 to 0.0290 cm^{-1} atm^{-1}, i.e. three times when J changes in the same range.[9] Results of calculations show that line shifts of H_2O molecule due to inert gas pressure depend weakly on the rotational quantum numbers.

Thus expression (11) allows one to calculate the average value of the line shift coefficient for specific band and to describe its vibrational dependence, as well as its dependence on perturbing atom polarizability. In particular, as follows from Eq. (12), shift depends nonlinearly on atom polarizability ($\delta \sim \alpha_2^{0.7}$), which completely explains its experimental dependence[5] for the $\nu_1 + 3\nu_3$ band of H_2O on buffer atom polarizability.

In Table I the calculated and experimental data on the line shift coefficients are presented, where δ_1 is the value calculated taking into account only the first order of the interruption function and using the Anderson interruption procedure; δ_{11} is the result of calculation using formula (11); δ_3 is line shift coefficient calculated taking into account corrections for bending of trajectory of light atoms (He and Ne). In the last column of Table I half–width values measured in Ref. 5 are presented. As is seen from the comparison of the measured and calculated values of the line shift coefficients, abandonment of the interruption procedure and refinement of the $S(b)$ dependence in the vicinity of $b = b_0$ significantly improves agreement with the experimental data for light atoms (He and Ne). For example, in case of H_2O–He mixture, shift is halved in comparison with the results of calculation by the ATC method. Usage of adjustment factors borrowed from Ref. 17 also improves agreement between calculated and measured values; there is good agreement even for light atoms (He and Ne).

In the present paper calculations have been performed for five buffer gases without adjustable parameters. The H_2O molecule polarizability in the upper vibrational state was determined earlier in Ref. 1 from the H_2O line shift due to air pressure. It should be noted that both present calculation and calculation for the H_2O line shifts due to N_2 (Ref. 1), SO_2 (Ref. 11), CO_2, and H_2O (Ref. 12) pressures performed earlier are in good agreement with the experiment; fitting procedure has been used in none of the calculations. Thus we can state that the relationship

$$C_6^{\,\mathrm{disp}} = \frac{3}{2}\,\bar{\varepsilon}\,\alpha_{\,H_2O}\,\alpha_2\ , \qquad (12)$$

following from the Unsöld approximation[14] and allowing us to estimate the dispersion energy seems to be suitable for line shift calculations. The approximation enables one to predict the line shifts caused not only by the pressure of polar molecules or molecules possessing intrinsic quadruple moments but also by rare gas pressure.

Applicability limits of Eq. (11) should be specified. Formula (11) includes the contribution coming from $S_1(b)$ only, i.e. the negative monotonic part of shift independent of the rotational quantum number J, but in so doing the oscillating component, i.e. the contributions coming from transitions whose frequencies differ in sign, are ignored. Consequently, this expression is applicable for line shift calculations for transitions into highly excited states on condition that perturbing particle possesses small permanent electric moment or no moment at all.

As an example, comparison of experimental average line shift coefficients and that calculated by formula (11) in the $3\nu_1 + \nu_3$ band is presented in Table III. As is seen, calculated average values for N_2, O_2, Ar, and Xe are in satisfactory agreement with the values obtained from experiments.[4,5,9,21] In the case in which the contribution from $S_2(b)$ exceeds contribution from $S_1(b)$ (for instance, for self–broadened water lines), the line shifts cannot be described by formula (11) and, as a result, calculated value in Table III differs significantly from experimental one.[22]

Table III. Mean values of line shift coefficients for H_2O *in the* $3\nu_1 + \nu_3$ *absorption band* ($cm^{-1} \cdot atm^{-1}$).

Buffer gas	Averaged over all lines (experiment)	Averaged over ten lines (experiment)	Mean value calculated by formula (11)
H_2O	+0.0037 (79 lines)	+0.0020	–0.0004
N_2	–0.0133 (64 lines)	–0.0110	–0.0077
O_2	–0.0261 (80 lines)	–0.0255	–0.0219
Ar	–0.0356 (80 lines)	–0.0342	–0.0351
Xe	–0.0363 (34 lines)	–0.03240	–0.0445

In calculations of line shifts caused by Xe pressure consideration must be given to the contribution of polarization interaction to $S_2(b)$ since Xe atom has large polarizability. Because present calculations ignore this contribution, there is no satisfactory agreement with experimental data for H_2O line shifts caused by Xe pressure in the $3\nu_1 + \nu_3$ band.[21]

Thus comparison between calculated and measured data on the H_2O absorption line shift coefficients caused by noble gas pressure in the $\nu_1 + 3\nu_3$ and $3\nu_1 + \nu_3$ bands shows the following. First, abandonment of the Anderson interruption approximation and introduction of correction for trajectory bending significantly improves the results of calculation and leads to agreement with the measured shift values. Second, the theoretical approach used in this paper allows us to derive a simple formula for the H_2O absorption line shift in the visible spectral region, which adequately describes the mean shift value for all measured lines in the band and considers its vibrational dependence.

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