

# Vibrational-rotational polarizability operator of asymmetric-top molecules. Effect on the shift and broadening of H<sub>2</sub>O molecular spectral lines

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Received July 10, 2002

A vibrational-rotational operator for the polarizability tensor of asymmetric-top molecules has been obtained by the methods of contact transformations. It has been shown that the rotational transformation gives no contributions being diagonal in the basis of symmetric-top rotational functions. The effect of the rotational dependence of the polarizability operator on the atomic argon pressure induced shift and broadening of rotational-vibrational spectral lines of the  $\nu_2$  band of the H<sub>2</sub>O molecule has been studied.

## Introduction

Knowledge of broadening and shift parameters of rotational-vibrational (RV) lines is important both for atmospheric applications and for studying intermolecular interaction forces. Numerical calculations of shift and broadening involve calculations of the matrix elements  $\langle \psi | A | \psi' \rangle$  of the operators  $A$  of different physical parameters, such as the molecular dipole moment  $\mu$ , polarizability  $\alpha$ , etc. Here  $\psi$  are rotational-vibrational wave functions of the molecular Hamiltonian  $H$ .

As a rule, rotational-vibrational energy levels and wave functions of molecules are calculated with the use of the transformed Hamiltonian  $\tilde{H} = U^+ H U$ , rather than the Hamiltonian  $H$  itself. The transformed Hamiltonian is obtained from  $H$  using the methods of contact transformations ( $U = \exp(-iS)$  is a unitary operator of a contact transformation). For asymmetric-top molecules, the wave functions  $\tilde{\Psi}$  are obtained through diagonalization of the Hamiltonian  $\tilde{H}$  in the symmetrized basis of RV wave functions. In this case, when calculating the matrix elements  $\langle \tilde{\Psi} | A | \tilde{\Psi}' \rangle$ , we have to pass on from  $\psi$  to  $\tilde{\Psi} = U^+ \psi$  and from the operators  $A$  to the transformed operators  $\tilde{A} = U^+ A U$  of physical parameters, i.e., to calculate the matrix element  $\langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi}' \rangle = \langle \psi | A | \psi' \rangle$ , and  $\tilde{A}$  should be obtained with the use of the same transformations that transform  $H$  into  $\tilde{H}$ . For the dipole moment  $\mu$  of asymmetric-top molecules, these transformations are considered in Refs. 1 and 2 (for semirigid molecules) and in Refs. 3 and 4 (for rigid asymmetric-top molecules).

In this paper, we, first, present the form of the rotational-vibrational polarizability operator of asymmetric-top molecules obtained by the method of contact transformations up to the second order of the perturbation theory. Second, we analyze the effect of the rotational dependence of this operator on Ar pressure-

induced shift and broadening of RV absorption lines of the H<sub>2</sub>O  $\nu_2$  band.

## 1. Calculation technique

The statistical polarizability tensor  $\alpha$  can be determined by Taylor series expansion of the dipole moment of a molecule in a stationary electric field about the field components  $F_\gamma$ :

$$\mu_\delta(F) = \mu_\delta + \sum_\gamma \alpha_{\delta\gamma} F_\gamma + \sum_{\gamma\eta} \beta_{\delta\gamma\eta} F_\gamma F_\eta + \dots \quad (1)$$

Here  $\alpha_{\delta\gamma}$  and  $\beta_{\delta\gamma\eta}$  are the components of the polarizability and hyperpolarizability tensor in the spatial coordinate system  $XYZ$ . If this system is chosen so that the axis  $Z$  is antiparallel to the electric field vector  $\mathbf{E}$ , then the contribution  $H_\alpha$  from the molecular dipole moment induced by the electric field  $\mathbf{E}$  to the total molecular Hamiltonian can be written as  $H_\alpha = \alpha_{ZZ} E^2$  ( $E = F_Z$ ). The components of  $\alpha$  in the molecular coordinate system are denoted as  $\alpha_{\beta\gamma}$  ( $\beta, \gamma = x, y, z$ ). It is convenient to pass on from  $\alpha_{\beta\gamma}$  to the irreducible tensor operators  $\alpha_{l,n}$  ( $l = 0, 2; n = 0$  for  $l = 0$  and  $n = 0, \pm 1, \pm 2$  for  $l = 2$ ). These operators are determined as

$$\begin{aligned} \alpha_{0,0} &= -(\alpha_{x,x} + \alpha_{y,y} + \alpha_{z,z})/\sqrt{3}, \\ \alpha_{2,0} &= (2\alpha_{z,z} - \alpha_{y,y} - \alpha_{x,x})/\sqrt{6}, \\ \alpha_{2,\pm 1} &= \mp(\alpha_{x,z} \pm i\alpha_{y,z}), \\ \alpha_{2,\pm 2} &= [(\alpha_{x,x} - \alpha_{y,y}) \pm 2\alpha_{x,y}]/2. \end{aligned} \quad (2)$$

The spatially fixed components  $W_\sigma^l$  of the tensor polarizability operator can be determined from the molecule-fixed components  $\alpha_{l,n}$  in an ordinary way:

$$\begin{aligned} W_{0,0}^0 &= D_{0,0}^0 \alpha_{0,0} = \alpha_{0,0}, \\ W_{\sigma,n}^2 &= \sum_n D_{\sigma,n}^2 \alpha_{2,n}. \end{aligned} \quad (3)$$

Here  $D_{\sigma,n}^l$  are rotational matrices.<sup>5,6</sup> Because of the chosen orientation of the spatial coordinate system,  $\sigma = 0$ . Consequently, from Eq. (2) we obtain that the component  $\alpha_{ZZ}$  can be written as  $\alpha_{ZZ} = \sqrt{6}/3 (W_0^2 - W_0^0/\sqrt{2})$  (see also Ref. 7). Note that only  $W_0^2$  depends on the spatial orientation of the molecule, while  $W_0^0$  is invariant about rotation. We assume that the molecule-fixed components  $\alpha_{\beta\gamma}$  depend on the normal coordinates  $q_i$  ( $i = 1, 2, 3$  for a triatomic nonlinear molecule  $X_2Y$ ), therefore  $\alpha_{\beta\gamma}$  can be Taylor series expanded about  $q_i$ :

$$\alpha_{\beta\gamma} = \alpha_{\beta\gamma}^0 + \lambda \sum_i \alpha_{\beta\gamma}^i q_i + \lambda^2 1/2 \sum_{i,j} \alpha_{\beta\gamma}^{ij} q_i q_j + \dots \quad (4)$$

Here  $\lambda$  is the bookkeeping parameter, which is commonly used in the theory of RV molecular spectra<sup>1,2</sup> to describe the expansion orders of different physical parameters with respect to the main contribution. For  $X_2Y$  molecules ( $C_{2v}$  symmetry), nonzero parameters in this series are:  $\alpha_{\beta\beta}^0$ ,  $\alpha_{\beta\beta}^i$ ,  $\alpha_{xz}^3$ ,  $\alpha_{\beta\beta}^{ij}$ , and  $\alpha_{xz}^{3i}$  ( $i, j = 1, 2$ ).

The molecule-fixed coordinate system is chosen so that the molecule is in the plane  $xz$  and the axis  $x$  is a bisector of the angle  $XYX$ . Substitution of Eq. (4) into Eq. (3) gives

$$W_0^l = {}^0W_0^l + \lambda {}^1W_0^l + \lambda^2 {}^2W_0^l + \dots, \quad (5)$$

where

$$\begin{aligned} {}^0W_0^l &= \sum_n D_{0,n}^l \alpha_{l,n}^0, \\ {}^1W_0^l &= \sum_n D_{0,n}^l \sum_i \alpha_{l,n}^i q_i, \\ {}^2W_0^l &= \sum_n D_{0,n}^l (1/2) \sum_{i,j} \alpha_{l,n}^{ij} q_i q_j, \\ &\dots \end{aligned} \quad (6)$$

The left superscript of  $W_0^l$  indicates the order of smallness of these operators. To calculate the transformed operator  $\tilde{W}_0^l$ , we use the same technique, as was used earlier to calculate the transformed dipole moment operator of asymmetric-top molecules in Refs. 1 and 2. The transformed operator  $\tilde{W}_0^l$  can be represented as

$$\begin{aligned} \tilde{W}_0^l &= U^+ W_0^l U = e^{iS} W_0^l e^{-iS} = \frac{1}{2} \sum_n \{D_{0,n}^l, \tilde{\alpha}_{l,n}\} = \\ &= {}^0\tilde{W}_0^l + \lambda {}^1\tilde{W}_0^l + \lambda^2 {}^2\tilde{W}_0^l + \dots = W_0^l + [iS, W_0^l] + \dots \quad (7) \end{aligned}$$

In this equation, braces denote anticommutator;  $\tilde{\alpha}_{l,n}$  are rotational-vibrational molecular polarizability operators, and  $S = \lambda S_1 + \lambda^2 S_2 + \dots$  is the operator of contact transformation. Up to the second order of smallness,

$$\begin{aligned} {}^0\tilde{W}_0^l &= {}^0W_0^l, \quad {}^1\tilde{W}_0^l = {}^1W_0^l, \\ {}^2\tilde{W}_0^l &= {}^2W_0^l + [iS_1^V, {}^1W_0^l]_V + [iS_1^R, {}^0W_0^l]_R. \quad (8) \end{aligned}$$

The symbols  $[iS_1^V, {}^1W_0^l]_V$  and  $[iS_1^R, {}^0W_0^l]_R$  denote the vibrational and rotational commutators. Here we follow the rule<sup>2</sup> that for any operator  $a$

$$[iS, a] = [iS, a]_V + \lambda [iS, a]_R,$$

i.e., the rotational commutator increases the order of smallness of the resultant term. For an asymmetric top  $S_1 = S_1^V + S_1^R$ , where  $S_1^V$  is an RV operator having the form<sup>1,2</sup>:

$$\begin{aligned} S_1^V &= \sum_{\alpha,\beta} J_\alpha J_\beta \sum_k S_k^{\alpha\beta} p_k + \sum_{kij} S^{kij} p_k p_i p_j + \\ &+ \sum_{kij} S_{ki}^j \frac{1}{2} (q_k q_i p_j + p_j q_k q_i) \quad (9) \end{aligned}$$

and

$$S_1^R = s_{111}^V (J_x J_y J_z + J_z J_y J_x) \quad (10)$$

is the rotational operator used in reducing of the asymmetric-top effective rotational Hamiltonian.<sup>1</sup> In these operators  $S_k^{\alpha\beta} = (-B_k^{\alpha\beta}/\omega_k)$ ;  $p_k = -i\partial/\partial q_k$ ;  $J_\alpha$  are the components of the molecular rotational operator in the molecular coordinate system;  $B_k^{\alpha\beta}$  are derivatives in the series expansion of the inverse inertia tensor about the normal coordinates;  $\omega_k$  are the frequencies of normal vibrations, and  $s_{111}^V$  is a parameter depending on the vibrational state and determined by the well-known equation.<sup>1,2</sup> The equations for  $S^{kij}$  and  $S_{ki}^j$  are given in Ref. 2. For  $l=0$  the last term in Eq. (8) is absent. Note that Eq. (8) accounts for only the contributions that are *diagonal* in the basis of vibrational wave functions, therefore in Eq. (9) there are no terms giving off-diagonal contributions (they depend on Coriolis constants).

## 2. Rotational-vibrational operators $\tilde{\alpha}_{l,n}$

According to Eqs. (4), (5), (7), and (8), the operators  $\tilde{\alpha}_{l,n}$  can be written as

$$\begin{aligned} \tilde{\alpha}_{l,n} &= \alpha_{l,n}^0 + \sum_i \alpha_{l,n}^i q_i + \frac{1}{2} \sum_{i,j} \alpha_{l,n}^{ij} q_i q_j + \\ &+ \Delta \tilde{\alpha}_{l,n}^V + \Delta \tilde{\alpha}_{l,n}^R. \quad (11) \end{aligned}$$

The last two terms in this equation are determined by the first and second commutators from Eq. (8). The first commutator is calculated trivially and gives

$$\begin{aligned} \Delta \tilde{\alpha}_{l,n}^V &= \sum_{\beta,\gamma} \Delta \alpha_{l,n}^{\beta\gamma} J_\beta J_\gamma + \Delta \alpha_{l,n}^{\text{vib}}, \\ \Delta \alpha_{l,n}^{\beta\gamma} &= \sum_k S_k^{\alpha\beta} \alpha_{l,n}^k, \quad (12) \end{aligned}$$

$$\Delta \alpha_{l,n}^{\text{vib}} = \sum_{i,j} (\Delta_1 \alpha_{l,n}^{ij} p_i p_j + \Delta_2 \alpha_{l,n}^{ij} q_i q_j).$$

The parameters  $\Delta_1\alpha_{l,n}^{ij}$  and  $\Delta_2\alpha_{l,n}^{ij}$  are connected with the derivatives for the polarizability tensor  $\alpha_{l,n}^i$  and the anharmonic constants  $\phi_{ijk}$  by the equations similar to those used in the theory of transformed molecular dipole moment operator, if the derivatives  $\alpha_{l,n}^i$  in them are replaced by the derivatives for the dipole moment.<sup>2</sup>

For calculation of the second commutator  $\Delta w_R = [iS_1^R, {}^0W_0^l]_R$  it is convenient to pass on to the spherical components  $J_\pm, J_z$  for the rotational operators<sup>8</sup> and to the functions  $D_{K,M}^J$ , which coincide with the symmetric-top rotational wave functions  $\Psi(JKM)$  accurate to a factor.<sup>6</sup> In this case

$$\Delta w_R = \left( -\frac{s_{111}^V}{2} \right) \left[ R - R^+, \sum_n (-1)^n D_{0,n}^{*l} \alpha_{l,-n} \right]_R, \quad (13)$$

where  $R = J_+^2(J_z + 1)$  and  $R^+$  is the Hermitian conjugate operator. Here we used the fact that  $D_{0,-n}^l = (-1)^n D_{0,n}^{*l}$ . The rules of action of the rotational operators  $J_\pm, J_z$  upon the rotational matrices  $D_{\sigma,n}^{*l}$  are well-known<sup>6</sup>:

$$J_\pm D_{\sigma,n}^{*l} = l_{l,n}^\pm D_{\sigma,n\pm 1}^{*l}, \quad J_z D_{\sigma,n}^{*l} = n D_{\sigma,n}^{*l}. \quad (14)$$

Here  $f_{l,n}^\pm = [(l \mp n)(l \pm n + 1)]^{1/2}$ . Application of the rules (14) gives

$$\begin{aligned} [R, D_{0,n}^{*l}] = & n J_+^2 D_{0,n}^{*l} - n f_{l,n}^+ J_+ D_{0,n+1}^{*l} - \\ & - \frac{1}{2} f_{l,n}^+ f_{l,n+1}^+ D_{0,n+2}^{*l} + f_{l,n}^+ \{ D_{0,n+1}^{*l}, J_+ (J_z + \frac{1}{2}) \}. \end{aligned} \quad (15)$$

This equation allows us to derive the rotational-vibrational operators  $\tilde{\alpha}_{l,n}$  for the polarizability tensor. For brevity, it is convenient to pass on to their linear combinations, which, for example, for  $X_2Y$  molecules have the form

$$\begin{aligned} \tilde{\alpha}_{l,0} = & \alpha_{l,0}^0 + \sum_i \alpha_{l,0}^i q_i + \frac{1}{2} \sum_i \alpha_{l,0}^{ij} q_i q_j + \\ & + \sum_\beta \Delta \alpha_{l,0}^{\beta\beta} J_\beta^2 + \Delta \alpha_{l,0}^{\text{vib}}, \\ \tilde{\alpha}_{2,1} - \tilde{\alpha}_{2,-1} = & -2\alpha_{x_2}^3 q_3 - \sum_i \alpha_{x_2}^{i3} q_i q_3 + s_{111}^V [2\Delta \alpha_{2,1}^{xz} + \\ & + 2(\alpha_{zz}^0 - \alpha_{xx}^0)] \{ J_x, J_z \} + 2\Delta \alpha_{2,1}^{\text{vib}}, \\ \tilde{\alpha}_{2,1} + \tilde{\alpha}_{2,-1} = & -[2is_{111}^V (\alpha_{zz}^0 - \alpha_{yy}^0)] \{ J_y, J_z \}, \quad (16) \\ \tilde{\alpha}_{2,2} + \tilde{\alpha}_{2,-2} = & 2\alpha_{2,2}^0 + 2 \sum_i \alpha_{2,2}^i q_i + \sum_i \alpha_{2,2}^{ij} q_i q_j + \\ & + 2 \sum_\beta \Delta \alpha_{2,2}^{\beta\beta} J_\beta^2 + 2\Delta \alpha_{2,2}^{\text{vib}}, \end{aligned}$$

$$\tilde{\alpha}_{2,2} - \tilde{\alpha}_{2,-2} = -4is_{111}^V \alpha_{2,2}^0 \{ J_x, J_y \}.$$

Here  $i, j = 1, 2; l = 0, 2$ .

### 3. Vibrational matrix elements

In calculation of the matrix elements  $\langle \tilde{\Psi} | \tilde{W}_0^l | \tilde{\Psi}' \rangle$ , we should use the wave functions  $\tilde{\Psi}$  obtained from diagonalization of the transformed molecular Hamiltonian. For orthorhombic molecules, these wave functions can be expressed through symmetrized wave functions, which are products of harmonic oscillator wave functions  $|\varphi_V\rangle = |V_1\rangle |V_2\rangle |V_3\rangle \dots$  and Wang functions.<sup>2</sup> For an isolated vibrational state  $\tilde{\Psi} = \varphi_V \varphi_{V,R}$ ,

where  $|\varphi_{V,R}\rangle = \sum_K C_K^V |J, K, \gamma\rangle$  are symmetrized rotational wave functions, in which the index  $\gamma = \pm 1$ ,  $R$  denotes a combination of rotational quantum numbers  $J, K_a, K_c$ , and the coefficients  $C_K^V$  follow from diagonalization of the effective rotational molecular Hamiltonian for the given vibrational state ( $V$ ).<sup>8</sup> The matrix elements  $\langle \tilde{\Psi} | \tilde{W}_0^l | \tilde{\Psi}' \rangle$  include vibrational matrix elements

$${}^{V,V'} \tilde{W}_0^l = \langle \varphi_V | \tilde{W}_0^l | \varphi_{V'} \rangle = \frac{1}{2} \sum_n \{ D_{n,0}^l, \tilde{\alpha}_{l,n}^{V,V'} \},$$

which depend on the rotational operators  $J_a$ . For the case  $V \neq V'$ , the square matrix elements  ${}^{V,V'} \tilde{W}_0^l$  (accurate to a factor) determine the line intensities in Raman spectra of the corresponding bands (isotropic part at  $l = 0$  and anisotropic part at  $l = 2$ ). For this case, we have to additionally calculate the contributions to  ${}^{V,V'} \tilde{W}_0^l$ , which are off-diagonal in the basis of vibrational wave functions. For  $V = V'$  the operators  ${}^{V,V} \tilde{W}_0^l = {}^V \tilde{W}_0^l$  are effective polarizability tensor operators for the given vibrational state ( $V$ ); the squares of these matrix elements enter into the equations for calculation of Raman line intensities corresponding to purely rotational transitions (actually, in these equations the first terms from Eq. (16) are kept, see, for example, Ref. 9; no publications are known to us, where the contributions depending on the parameters of the contact transformation operator to the effective polarizability tensor are taken into account in calculation of line intensities in Raman spectra of asymmetric-top molecules). The coefficients  $\tilde{\alpha}_{l,n}^V = \tilde{\alpha}_{l,n}^{V,V'}$  of  $D_{n,0}^l$  determine the effective polarizability of the molecule. From Eqs. (16) we can easily obtain the equations for the corresponding combinations

$$\begin{aligned} \tilde{\alpha}_{l,0}^V = & \alpha_{l,0}^V + \sum_\beta \Delta \alpha_{l,0}^{\beta\beta} J_\beta^2, \\ \tilde{\alpha}_{2,1}^V - \tilde{\alpha}_{2,-1}^V = & s_{111}^V [2\Delta \alpha_{2,1}^{xz} + 2(\alpha_{zz}^0 - \alpha_{xx}^0)] \{ J_x, J_z \}, \end{aligned}$$

$$\begin{aligned}
\tilde{\alpha}_{2,1}^V + \tilde{\alpha}_{2,-1}^V &= -[2is_{111}^V(\alpha_{zz}^0 - \alpha_{yy}^0)]\{J_y, J_z\}, \\
\tilde{\alpha}_{2,2}^V + \tilde{\alpha}_{2,-2}^V &= 2\alpha_{2,2}^V + 2\sum_{\beta} \Delta\alpha_{2,2}^{\beta\beta} J_{\beta}^2, \\
\tilde{\alpha}_{2,2}^V - \tilde{\alpha}_{2,-2}^V &= -4is_{111}^V\alpha_{2,2}^0\{J_x, J_y\}. \quad (17)
\end{aligned}$$

Here

$$\alpha_{l,n}^V = \alpha_{l,n}^0 + \frac{1}{2} \sum_i (V_i + \frac{1}{2}) \left( \alpha_{l,n}^{ii} - \frac{1}{2} \sum_k \frac{\alpha_{l,n}^k \phi_{kii}}{\omega_k} \right),$$

$l = 0, 2; n = 0, 2.$

#### 4. Average rotational-vibrational polarizability

In the theory of spectral line shifts and broadening induced by the buffer gas pressure, when calculating the matrix elements  $\langle \tilde{\Psi} | \tilde{W}'_0 | \tilde{\Psi}' \rangle$ , it is sufficient to restrict the consideration to the case that matrix elements are diagonal in the basis of vibrational wave functions. Keeping only average, or effective, values of polarizability in the given vibrational-rotational state in these matrix elements, we obtain

$$\langle \tilde{\Psi} | \tilde{W}'_0 | \tilde{\Psi}' \rangle = \sum_n \langle \varphi_{V,R} | D'_{n,0} | \varphi'_{V,R} \rangle \tilde{\alpha}_{l,n}^V(R, R'),$$

where

$$\tilde{\alpha}_{l,n}^V(R, R') = (\tilde{\alpha}_{l,n}^V(R) + \tilde{\alpha}_{l,n}^V(R')) / 2$$

and

$$\tilde{\alpha}_{l,n}^V(R) = \langle \varphi_{V,R} | \tilde{\alpha}_{l,n}^V | \varphi_{V,R} \rangle.$$

The parameters  $\tilde{\alpha}_{l,n}^V(R)$  are the effective molecular polarizabilities in the given RV state. The matrix elements of  $D$ -functions in the basis of rotational wave functions  $\varphi_{V,R}$  are known with the known coefficients  $C_K^V$  for  $\varphi_{V,R}$ . It is seen from Eqs. (17) that no contributions to  $\tilde{\alpha}_{l,n}^V(R)$  include the parameter  $s_{111}^V$ , i.e., the rotational contact transformation does not contribute to the effective average values for the polarizability tensor. It also follows from these equations that  $\tilde{\alpha}_{2,2}^V(R) = \tilde{\alpha}_{2,-2}^V(R)$ . Determine ordinary combinations for  $\Delta\alpha_{l,n}^{\beta\beta}$  at  $l = 0, 2, n = 0, 2$ :

$$\begin{aligned}
\Delta\alpha_{l,n}^J &= (\Delta\alpha_{l,n}^{xx} + \Delta\alpha_{l,n}^{yy}) / 2, \\
\Delta\alpha_{l,n}^K &= \Delta\alpha_{l,n}^{zz} - \Delta\alpha_{l,n}^J, \\
\Delta\alpha_{l,n}^C &= (\Delta\alpha_{l,n}^{xx} - \Delta\alpha_{l,n}^{yy}) / 2.
\end{aligned}$$

Then

$$\begin{aligned}
\tilde{\alpha}_{l,n}^V(R) &= \alpha_{l,n}^V + \Delta\alpha_{l,n}^J J(J+1) + \Delta\alpha_{l,n}^K \sum_K C_K K^2 + \\
&+ (\Delta\alpha_{l,n}^C / 2) (\sum_K C_K C_{K+2} E(K, K+2) Z_K + \gamma C_1^2 \delta_{K,1}). \quad (18)
\end{aligned}$$

Here  $Z_K = 1$  at  $K \neq 0$  and  $Z_K = 1/\sqrt{2}$  at  $K = 0$ ;  $E(K, K+2) = f_{J,K}^+ f_{J,K+1}^+$  and  $\delta_{K,1}$  is delta symbol.

#### 5. Calculation of Ar pressure induced shifts and broadening of lines of the H<sub>2</sub>O $\nu_2$ band

For the system H<sub>2</sub>O-X (X are atoms of inert gases), line shift and broadening are determined by the dispersion part of the intermolecular interaction Hamiltonian, therefore just for such mixtures it is convenient to analyze the effect on the parameters  $\gamma$  (line halfwidth) and  $\delta$  (line shift). The parameters  $\gamma_{if}$  and  $\delta_{if}$  for the transition ( $i \rightarrow f$ ) in this case are determined (see, for example, Refs. 10 and 11) in the following way:

$$\gamma_{if} + i\delta_{if} = (n/c) (\text{Re}\sigma + i\text{Im}\sigma), \quad (19)$$

where

$$\sigma = \int_0^{\infty} v F(v) dv \int_0^{\infty} S(b) b db. \quad (20)$$

In Eq. (19)  $n$  is the concentration of buffer gas molecules;  $c$  is the speed of light;  $v$  is the relative velocity of colliding particles, and  $S(b) = S_1(b) + S_2(b) + \dots$  is the interruption function depending on  $v$ . In the Robert-Bonamy calculation,<sup>12</sup> used in this work,

$$\begin{aligned}
\text{Re}S(b) &= 1 - e^{-\text{Re}S_2(b)} \cos(\theta_1 + \theta_2); \\
\text{Im}S(b) &= e^{-\text{Re}S_2(b)} \sin(\theta_1 + \theta_2). \quad (21)
\end{aligned}$$

In these equations

$$\begin{aligned}
\text{Re}S_2(b) &= \text{Re}(S_{2,i}^{\text{outer}} + S_{2,f}^{\text{outer}}) + S_2^{\text{middle}}; \\
\theta_2 &= \text{Im}(S_{2,i}^{\text{outer}} - S_{2,f}^{\text{outer}}),
\end{aligned}$$

and

$$\begin{aligned}
\theta_1 = S_1(b)/i &= -\frac{3\pi}{8(\hbar v)b^5} \{ \mu^2(i) - \mu^2(f) + \\
&+ \frac{3}{2} \bar{u} [\alpha(i) - \alpha(f)] \} \alpha_2. \quad (22)
\end{aligned}$$

Here  $\alpha_2$  is the polarizability of Ar atom,  $\bar{u} = u_1 u_2 / (u_1 + u_2)$  ( $u_1, u_2$  are ionization potentials of the molecule and the atom), and  $\mu(i), \alpha(i)$  are diagonal matrix elements of the molecular dipole moment and average polarizability operators by RV wave functions. Consequently, they are the effective values of the dipole moment and polarizability in this RV state, that is,  $\mu(i) = \mu^V(J, K_a, K_c)$  and  $\alpha(i) = (-1/\sqrt{3}) \tilde{\alpha}_{0,0}^V(R) = (-1/\sqrt{3}) \tilde{\alpha}_{0,0}^V(J, K_a, K_c)$ . Here  $i$  is the generalized quantum number consisting of the set of vibrational  $V = \{V_1, V_2, \dots\}$  and rotational  $R = \{J, K_a, K_c\}$  quantum numbers.

The functions  $S_{2,i}^{\text{outer}}, S_{2,f}^{\text{outer}}$ , and  $S_2^{\text{middle}}$  consist of terms including (in the designations of Ref. 11)

matrix elements of the type of  $C_{20}^{(11;11)}(i2, i'2)$ ,  $C_{20}^{(11;11)}(f2, f'2)$ , i.e., the main contribution  ${}^{2,0}S_2$  is taken into account in the series expansion of the function  $S_2$  about the types of interaction. Using Eqs. (2.14) and (3.3) from Ref. 11, we can find

$$C_{20}^{(11;11)}(i2, i'2) = (2J_i + 1)^{1/2} \times \sum_n u_{2,n}(i, i') \langle i' || D_n^2 || i \rangle. \quad (23)$$

Here  $\langle i' || D_n^2 || i \rangle$  are reduced matrix elements, and

$$u_{2,n}(i, i') = (\sqrt{3}/2)\alpha_2[u\alpha_{2,0}(i, i') + (1/\sqrt{6})\mu^2(i, i')], \\ u_{2,2}(i, i') = u_{2,-2}(i, i') = \\ = (\sqrt{3}/2)\alpha_2[u\alpha_{2,2}(i, i') - \mu^2(i, i')/2] \quad (24)$$

and

$$\alpha_{l,n}(i, i') = \tilde{\alpha}_{l,n}^V(R, R').$$

To calculate the parameters  $\tilde{\alpha}_{l,n}^V(J, K_a, K_c)$  by Eqs. (17), we have to know the first and second derivatives of all components of the polarizability tensor. The derivatives can be either found in quantum-chemical calculations or reconstructed from experimental intensities of Raman lines (the reconstruction technique and results for some molecules are given in Ref. 9). In Ref. 13, the average polarizabilities  $\alpha$  of the H<sub>2</sub>O molecule for the first five (in energy) vibrational states were obtained in quantum-chemical calculations. The vibrational dependence obtained can be described by the following equation (in atomic units):

$$\alpha = 9.86 + 0.29V_1 + 0.03V_2 + 0.28V_3. \quad (25)$$

On the other hand, from analysis of the nitrogen pressure induced shift coefficients for water vapor absorption lines in Refs. 14 and 15, the values of the average polarizability of the H<sub>2</sub>O molecule for a large number of vibrational states were obtained; for these values the following equation is given in Ref. 15:

$$\alpha = (14.69 + 0.2919V_1 + 0.4782V_2 + \\ + 0.3725V_3 - 0.1702V_2^2) \cdot 10^{-25} \text{ cm}^3. \quad (26)$$

Note that for the state (010) Eqs. (25) and (26) lead to different values of the average polarizability  $\alpha$ , and this difference is significant in calculation of line shifts in the band considered.

In this paper we present the calculation of the coefficients  $\gamma_{if}$  and  $\delta_{if}$  induced by the Ar pressure for the  $\nu_2$  band of the H<sub>2</sub>O molecule depending on the effective parameters  $\alpha_{0,0} = (-1/\sqrt{3})\alpha$ ,  $\alpha_{2,0}$ , and  $\alpha_{2,2}$  (all in <sup>3</sup>).

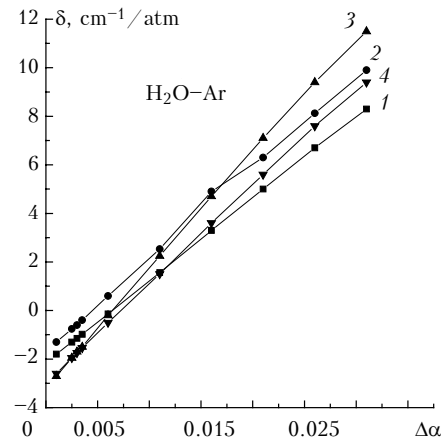
Since these parameters include corrections for the rotational dependence [Eq. (18)], this calculation allows

us to judge the effect of the rotational dependence on the line shift and broadening. For calculation we took two groups of lines ( $J K_a K_c \rightarrow J' K'_a K'_c$ ). The first group consists of four lines with different values of the quantum numbers  $J, J'$  and small  $K_a, K'_a$ . They are the following: (3 1 2)  $\rightarrow$  (4 4 1) (line 1,  $\gamma = 36.0$ ), (8 1 8)  $\rightarrow$  (9 2 7) (line 2,  $\gamma = 30.0$ ), (12 1 11)  $\rightarrow$  (11 2 10) (line 3,  $\gamma = 7.7$ ), and (15 1 15)  $\rightarrow$  (16 0 16) (line 4,  $\gamma = 3.7$ ). Given in parenthesis is the experimental value of the parameter  $\gamma$  in  $10^{-3} \text{ cm}^{-1}/\text{atm}$  from Ref. 15.

The second group is formed by lines with  $J = 8, J' = 9$  and different  $K_a, K'_a$ : line 2, line 5 ((8 5 3)  $\rightarrow$  (9 6 4),  $\gamma = 16.9$ ), line 6 ((8 6 2)  $\rightarrow$  (9 7 3),  $\gamma = 13.4$ ), and line 7 ((8 6 3)  $\rightarrow$  (9 7 2),  $\gamma = 13.3$ ). The dependence of the water vapor dipole moment on rotational quantum numbers was calculated using the parameters from Ref. 4.

First, we have calculated  $\gamma_{if}$  and  $\delta_{if}$  depending on the difference  $\Delta\alpha = \alpha(i) - \alpha(f)$ , which can be presented for the first group of lines as  $\Delta\alpha \approx (-1/\sqrt{3})[\alpha_{0,0}^{(000)} - \alpha_{0,0}^{(010)} - 2\Delta\alpha_{0,0}^J(J+1)]$ . The calculation has shown that the parameters  $\gamma_{if}$ , as would be expected, are almost independent of  $\Delta\alpha$ , while the line shifts  $\delta_{if}$  significantly depend on  $\Delta\alpha$ .

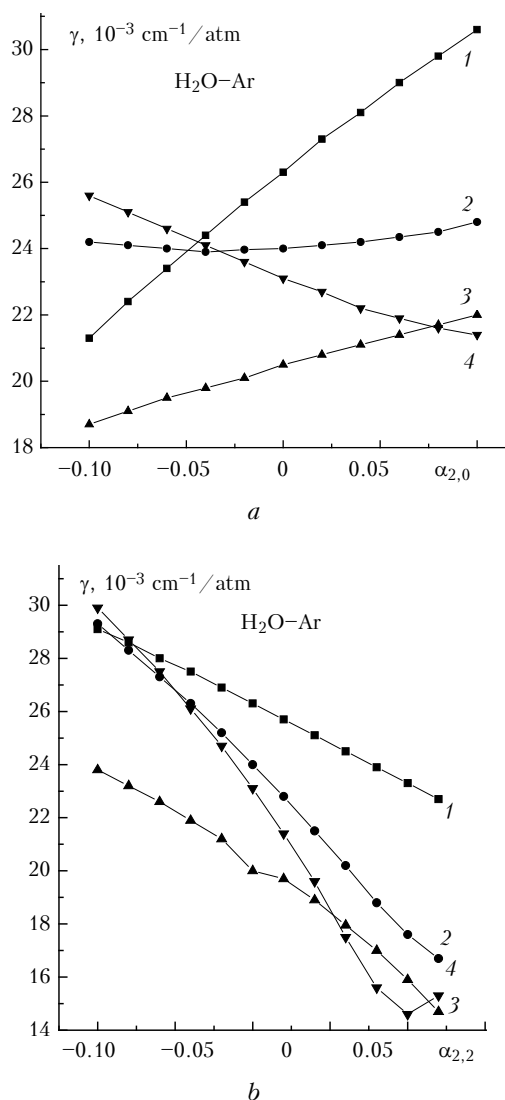
This dependence is shown in Fig. 1. Almost the same behavior of the shifts for all the first-group lines (regardless of  $J$  and  $J'$ ) shows that the parameter  $\Delta\alpha_{0,0}^J$  from Eq. (18) is insignificant for calculation of  $\gamma_{if}$  and  $\delta_{if}$ . The behavior of  $\delta_{if}$  can be described by the vibrational dependence of the mean polarizability. Note that at  $\Delta\alpha = 0.0045$  corresponding to  $\alpha^{(010)}$  calculated by Eq. (25), the line shifts are close to zero or negative, and for  $\Delta\alpha = 0.036$  corresponding to the calculation by Eq. (26), the line shifts are positive.



**Fig. 1.** Calculated dependence of line shifts for the  $\nu_2$  band of the water molecule induced by the argon pressure on the difference  $\alpha(i) - \alpha(f)$  of the average H<sub>2</sub>O polarizability. Curve 1 corresponds to the line (3 1 2)  $\rightarrow$  (4 4 1), curve 2 – line (8 1 8)  $\rightarrow$  (9 2 7), curve 3 – line (12 1 11)  $\rightarrow$  (11 2 10), curve 4 – line (15 1 15)  $\rightarrow$  (16 0 16).

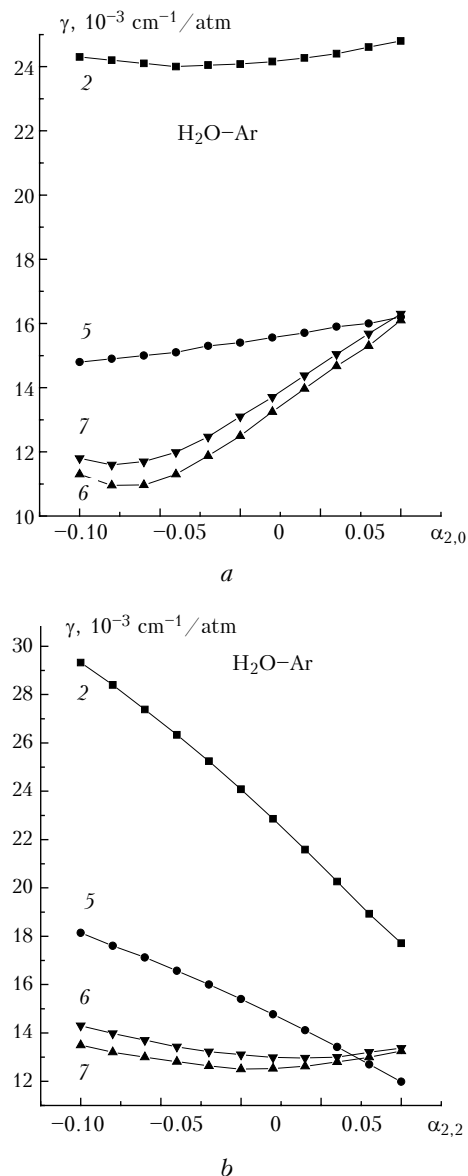
Figure 2 depicts the calculated dependences of the halfwidths  $\gamma_{if}$  for the first group of lines on the

parameters  $\alpha_{2,0}$  and  $\alpha_{2,2}$  ( $\alpha^{(000)} = 1.469$ ,  $\alpha^{(010)} = 1.473$ , in the first case  $\alpha_{2,2}$  is fixed to zero, and in the second case  $\alpha_{2,0} = 0$ ). As can be seen, the lines with different  $J$  and  $J'$  differently depend on these parameters. This means that the parameters  $\Delta\alpha_{2,0}^J$  and  $\Delta\alpha_{2,2}^J$  from Eq. (18) significantly affect the calculated values of  $\gamma_{if}$  (they almost do not affect the shifts). To be noted is also the poor agreement between the calculated and the experimental values of  $\gamma_{if}$  for the lines with large  $J$  and  $J'$ .



**Fig. 2.** Calculated dependence of the halfwidths of the H<sub>2</sub>O first-group lines (see Fig. 1) on the polarizability components  $\alpha_{2,0}$  (a) and  $\alpha_{2,2}$  (b).

The similar calculation for the second-group lines is shown in Fig. 3. The calculation shows that the lines with different  $K_a$  and  $K'_a$  differently depend on the parameters  $\alpha_{2,0}$  and  $\alpha_{2,2}$  and, consequently, the parameters  $\Delta\alpha_{2,0}^K$  and  $\Delta\alpha_{2,2}^K$  are important in calculation of halfwidths of these lines.



**Fig. 3.** Calculated dependence of the halfwidths of the H<sub>2</sub>O second-group lines on the polarizability components  $\alpha_{2,0}$  (a) and  $\alpha_{2,2}$  (b). Curve 2 – line (8 1 8) → (9 2 7), curve 5 – line (8 5 3) → (9 6 4), curve 6 – line (8 6 2) → (9 7 3), and curve 7 – line (8 6 3) → (9 7 2).

## Conclusion

The main result of this work is, first, derivation of the transformed polarizability tensor operator for asymmetric-top molecules, Eqs. (17) and (18), in which the contributions (accurate to the second order of the perturbation theory) following from contact transformations are determined. The equations obtained can be used to calculate the intensities of RV lines in Raman spectra of molecules or to determine the first derivatives of the polarizability components in the normal coordinates, as it is done in the theory of absorption line intensity.<sup>2</sup>

The second result is connected with the analysis of the effect of the contributions to the polarizability tensor components, that follow from contact transformations, on the pressure-induced shift and broadening of lines of the H<sub>2</sub>O  $\nu_2$  band. The analysis is performed in the Robert–Bonamy formalism, which ignores the effect of deviation from a straight-line trajectory. In this connection, we did not try to determine the optimal values of  $\Delta\alpha_{l,n}^J$  and  $\Delta\alpha_{l,n}^K$ , giving the closest agreement with the experiment. The analysis shows that the allowance for the rotational dependence in the effective operators for the polarizability tensor can lead to changes in the values calculated for halfwidths. These changes may be comparable with the changes resulting from the allowance for other interaction mechanisms, in particular, the allowance for the atom-atom potential or trajectory bending (as in the Robert–Bonamy calculation).

### Acknowledgments

The authors are thankful to Dr. S.N. Mikhailenko, Prof. Yu.N. Ponomarev, and Dr. I.V. Ptashnik for the help and attention to this work.

### References

1. M.R. Aliev and J.K.G. Watson, in: *Molecular Spectroscopy. Modern Research* (Academic Press, 1985), Vol. 3, pp. 1–67.
2. C. Camy-Peyret and J.M. Flaud, in: *Molecular Spectroscopy. Modern Research* (Academic Press, 1985), Vol. 3, pp. 70–117.
3. V.I. Starikov and S.N. Mikhailenko, *Atmos. Oceanic Opt.* **5**, No. 2, 82–87 (1992).
4. V.I. Starikov, *J. Mol. Spectrosc.* **206**, No. 2, 166–171 (2001).
5. M. Tinkham, *Group Theory and Quantum Mechanics* (Mc.Graw-Hill, New York, 1964).
6. L.C. Biedenharn and J.D. Louck, *Angular Momentum in Quantum Physics: Theory and Application* (Addison-Wesley, Reading, MA, 1981).
7. M. Mengel and P.A. Ensen, *J. Mol. Spectrosc.* **169**, No. 1, 73–91 (1995).
8. Yu.S. Makushkin and V.I.G. Tyuterev, *Perturbation Methods and Effective Hamiltonians in Molecular Spectroscopy* (Nauka, Novosibirsk, 1984), 240 pp.
9. A. Weber, *Raman Spectroscopy of Gases and Liquids* (Springer-Verlag, New York, 1979).
10. C.J. Tsao and B. Curnutte, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 41–92 (1961).
11. R.P. Leavitt, *J. Chem. Phys.* **73**, No. 11, 5432–5450 (1980).
12. D. Robert and J. Bonamy, *J. de Physique* **40**, No. 10, 923–943 (1979).
13. A.D. Bykov, B.E. Grossman, E.V. Browell, V.A. Kapitanov, E.A. Korotchenko, V.V. Lazarev, Yu.N. Ponomarev, L.N. Sinitsa, V.N. Stroinova, and B.A. Tikhomirov, *Atm. Opt.* **3**, No. 7, 617–630 (1990).
14. A.D. Bykov, N.N. Lavrent'va, and L.N. Sinitsa, *Opt. Spectrosc.* **83**, No. 1, 73–82 (1997).
15. C. Claveau, A. Henry, D. Hurtmans, and F. Valentin, *J. Quant. Spectrosc. Radiat. Transfer* **68**, 273–298 (2001).