# AN EFFECTIVE DIPOLE MOMENT OPERATOR FOR NONRIGID $H_2X$-TYPE MOLECULES. APPLICATION TO $H_2O$ MOLECULE

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*A theory of effective dipole moment of nonrigid molecules of $H_2X$–type is developed. A large amplitude vibration described by the* $\rho$ *coordinate is taken into account. Based on solution of inverse problem and model representation the function* $\mu_x^e(\rho)$, $\mu_x^1(\rho)$, *and* $\mu_x^3(\rho)$ *for $H_2O$ molecule is reconstructed from the series expansion of the molecular dipole moment over normal coordinates* $q_i\,(i = 1,3)$.

## INTRODUCTION

A theoretical study of the intensity of rovibrational absorption lines of molecules needs for calculating matrix elements of the effective dipole moment on the basis of rovibrational wave functions corresponding to the zeroth approximation of the Hamiltonian of a molecule (or on the basis of rovibrational wave functions obtained using the perturbation theory). In addition, information about these matrix elements can be obtained from experimentally measured intensities of absorption lines. This paper is devoted to investigation of the dipole moment function of the $H_20$ molecule based on experimental data on the parameters of the effective dipole moment presented in Refs. 1–7 and using theoretical relations connecting these parameters with the function of dipole moment and the parameters of rovibrational Hamiltonian $H$ of a nonrigid molecule.[8] In Ref. 9 such theoretical relations have been derived for asymmetric top molecules assuming the molecular vibrations to be small (i.e. on the basis of harmonic wave functions).

## GENERAL RELATIONS FOR THE OPERATOR OF EFFECTIVE DIPOLE MOMENT

A transformed operator of dipole moment $\mu_Z'$ (only Z–component of the operator $\mu$ in the spatial coordinate system is given by

$$\mu_Z' = \mu_Z + [iS,\ \mu_Z] + \frac{1}{2}[iS,\ [iS,\ \mu_Z]] + \ldots, \qquad (1)$$

where $iS$ is the operator of a contact vibrational transformation of the initial Hamiltonian $H$ of a molecule into an effective rotational Hamiltonian $H^{\text{eff}}$. By a rotational contact transformation the operator $\mu_Z'$ is reduced to the operator of effective dipole moment

$$\tilde{\mu}_Z = \mu_Z' + [i^RS,\ \mu_Z'] + \ldots . \qquad (2)$$

The above relations are exactly the same as those used in the model of a quasirigid molecule.[9] The main difference between the calculations made in Ref. 9 and ours presented below are the following. First, the functions $\mu_\alpha(\rho,\ q_i)$ i.e., the components of the dipole moment д in the molecular coordinate system ($\alpha = x,\ y,\ z$) related to $\mu_Z$ by

$$\mu_Z = \sum_\alpha \varphi_\alpha \mu_\alpha ,$$

where $\varphi_\alpha$ are the direction cosines, are expanded in a series only over $q_i$ that correspond to small amplitude vibrationson

$$\mu_\alpha(\rho,\ q_i) = \mu_a^e(\rho) + \sum_i \mu_\alpha^i(\rho,\ q_i) + \frac{1}{2}\sum_{ij} \mu_\alpha^{ij}(\rho)\, q_i\, q_j + \ldots,$$
$$i,j = 1,\ 3. \qquad (3)$$

The coefficients of the series expansion (3) are functions of the strong vibration coordinate $\rho$ (see Ref. 8). For the second, the basis of vibrational wave functions is composed of the functions $\psi_n(\rho)\cdot\varphi_\nu(q)$, where $\varphi_\nu(q)$ are eigenfunctions of the Hamiltonian $H_0^{sm.vib}$ that describes harmonic oscillations in the molecule, and $\psi_n(\rho)$ are the wave functions obtained by integrating numerically the Schrödinger wave equation.[10]

$$H_0^b\ \psi_n(\rho) =$$
$$= \left\{-B_\rho(\rho)\frac{\partial^2}{\partial\rho^2} - \left[\frac{\partial}{\partial\rho}B_\rho(\rho)\right]\frac{\partial}{\partial\rho} + U_0(\rho) + V_0(\rho)\right\}\Psi_n(\rho) = E_n\psi_n(\rho) \qquad (4)$$

with the anharmonic potential function $V_0(\rho)$. The zeroth approximation Hamiltonian,

$$H_0 = H_0^{sm.vib}(q)\ H_0^b \qquad (5)$$

that is used when transforming the initial Hamiltonian $H$ of a nonrigid molecule to the effective one $H^{\text{eff}}$ results from the expansions of the potential function $V(\rho,\ q_i)$ and of the inverse inertia tensor $\mu_{\alpha\beta}(\rho,\ q_i)$ into series $q_i$ coordinates

$$V(\rho,\ q_i) = V_0(\rho) + \sum_i \phi_i(\rho)\, q_i +$$
$$+ \frac{1}{2}\sum_{ij}\{\omega_i(\rho)\,\delta_{ij} + \phi_{ij}(\rho)\}\, q_i\, q_j + \frac{1}{6}\sum_{ijl}\phi_{ijl}(\rho)\, q_i\, q_j q_l + \ldots; \qquad (6a)$$

$$\frac{1}{2}\mu_{\alpha\beta}(\rho,\ q_i) = B_\alpha(\rho)\,\delta_{\alpha\beta} + \sum_i B_i^{\alpha\beta}(\rho) q_i + \sum_{ij} B_{ij}^{\alpha\beta}(\rho) q_i q_j + \ldots . \qquad (6b)$$

The scheme of calculations of operators of $iS$ transformations within the model of a nonrigid molecule and using the zeroth approximation of $H_0$ (Eq. 5) can be found in Ref. 11, and the generator $i^RS$ is described in Ref. 9, therefore we omit detailed derivation of individual contributions to $\tilde{\mu}_Z$ on the basis of vibrational wave functions. We should like to note only that all below calculations were performed to the terms of the second order of the small parameter $K \cong (\bar{B}/\bar{\omega})$ magnitude, where $\bar{B}$ is the mean rotational constant and $\bar{\omega}$ is the mean frequency of a harmonic oscillation. For the sake of convenience we shall reduce these matrix elements to the form similar to that described in Ref. 9, while, in contrast to Ref. 9, we use different relation of these matrix elements to the molecular parameters and parameters of dipole moment function.

## AN EFFECTIVE DIPOLE MOMENT OF A MOLECULE IN A GIVEN VIBRATIONAL STATE

Let us write, according to Ref. 9, this matrix element in the form

$$\tilde{\mu}_Z(n,v) = \langle n, v \,|\, \tilde{\mu}_Z \,|\, v, n\rangle = \sum_{\alpha} \varphi_\alpha \tilde{\mu}^e_a(n,v) +$$

$$+ \sum_{\alpha\beta\gamma} \frac{1}{2}\{\varphi_\alpha, J_\beta J_\gamma\}^{\alpha,\beta,\gamma}\tilde{M}_2(n), \tag{7}$$

where $|n, v\rangle = |\Psi_n\rangle |\varphi_{v_1}\rangle |\varphi_{v_3}\rangle$, $\{A, B\} = AB + BA$.

For parameters $\tilde{\mu}^e_a(n, v)$ and ${}^{\alpha,\beta,\gamma}\tilde{M}_2(n)$ we have obtained the relations

$$\tilde{\mu}^e_\alpha(n, v) = \mu^e_\alpha(n) + \sum_k \left(v_k + \frac{1}{2}\right)\left\{\frac{1}{2}\mu^{kk}_\alpha(n) - \right.$$

$$\left. -\frac{1}{4}\sum_i \frac{\mu^i_\alpha(n)\,\phi_{ikk}(n)}{\omega_i} - \sum_s \frac{\tilde{\phi}_{kk}(ns)\,\mu^e_\alpha(sn)}{\Omega_{sn}}\right\}. \tag{8}$$

$$^{\alpha,\beta\gamma}\tilde{M}_2(n) = 2\sum_s \frac{B_\beta(ns)\,\mu^e_\alpha(sn)}{\Omega_{ns}}\delta_{\beta\gamma} - \sum_s \frac{B^{\beta\gamma}_k(n)\,\mu^k_\alpha(n)}{\omega_k} +$$

$$+ S^{(n)}_{111}\sum_\delta \varepsilon_{\beta\gamma\delta}\left(\delta_{\alpha\gamma}\mu^e_\beta(n) - \delta_{\alpha\beta}\mu^e_\gamma(n)\right), \tag{9}$$

where $f(nm) = \langle\Psi_n | f(\rho) | \Psi_m\rangle$, $f(n) = f(nn)$, $\varphi_{\kappa\kappa}(\rho) = \varphi_{\kappa\kappa}(\rho) + 2\Delta\omega_\kappa(\rho)$, $\Delta\omega_\kappa(\rho) = \omega_\kappa(\rho) - \omega_\kappa(\rho_e)$, $\Omega_{nS} = E_n - E_s$, and $\varepsilon_{\alpha\beta\gamma}$ is tne antisymmetric unit tensor of the third rank. The relation of the parameter $S^{(n)}_{11}$ to the parameters of effective Hamiltonian remains the same as in the model of a semirigid molecule,[12] while the relation of the latter to the molecular parameters is different.[13,14] In the limiting case of a simmgid molecule the following series expansions are valid:

$$\mu^e_\alpha(\rho) = \mu^e_\alpha(\rho_e) + \left.\frac{\partial\mu_\alpha}{\partial q_2}\right|_{\rho_e} \cdot q_2 + \ldots;$$

$$B_\alpha(\rho) = B_\alpha(\rho_e) + \left.\frac{\partial B_\alpha}{\partial q_2}\right|_{\rho_e} \cdot q_2 + \ldots, \quad q_2 = \kappa(\rho - \rho_e) \tag{10}$$

as well as similar expansions of the functions $\mu^i_\alpha(\rho)$, $B^{\alpha\beta}_\kappa(\rho)$, ... . The enharmonic wave functions $|n\rangle$ may be represented in series expansions over the functions of harmonic oscillator $|m\rangle_0$

$$|n\rangle = |n\rangle_0 + \frac{1}{6}\sum_m \frac{{}_0\langle m | \phi_{222}\cdot q_2^3 | n\rangle_0}{(n-m)\omega_2}|m\rangle_0 + \ldots . \tag{11}$$

Substitution of relations (10) and (11) in formulas (8) and (9) yields the well-known relations derived in Ref. 9.

## AN EFFECTIVE DIPOLE MOMENT RELATING BENDING VIBRATIONAL STATES

The sought-after-matrix element is given by

$$\tilde{\mu}_Z(nm) = \langle n, v = 0 \,|\, \tilde{\mu}_z \,|\, v = 0, \cdot m\rangle =$$

$$= \sum_\alpha \varphi\alpha\,\tilde{\mu}_\alpha(nm) - i\sum_{\alpha\beta}\frac{1}{2}\{\varphi_\alpha, J_\beta\}^{\alpha,\beta}\tilde{M}_2(nm). \tag{12}$$

For coefficients $\tilde{\mu}_\alpha(nm)$ and ${}^{\alpha,\beta}\tilde{M}_2(mn)$ we have obtained the relations

$$\tilde{\mu}_\alpha(nm) = \mu^e_\alpha(nm) +$$

$$+\frac{1}{2}\sum_s{}^{*}\sum_i\left\{\frac{\tilde{\Phi}_i(ns)\,\mu^i_\alpha(sm)}{\Omega_{ns}-\omega_i} + \frac{\mu^i_\alpha(ns)\,\tilde{\Phi}_i(sm)}{\Omega_{ms}-\omega_i}\right\} +$$

$$+\frac{1}{4}\sum_s\sum_k\left\{\frac{\tilde{\Phi}_{kk}(ns)\,\mu^e_\alpha(sm)}{\Omega_{ns}} + \frac{\mu^e_\alpha(ns)\,\tilde{\Phi}_{kk}(sm)}{\Omega_{ms}}\right\}; \tag{13}$$

$$^{\alpha,\beta}\tilde{M}_2(nm) = i\sum_s{}^{*}\sum_k\left\{\frac{T^\beta_k(ns)\,\mu^k_\alpha(sm)}{\Omega_{ns}-\omega_k} + \frac{\mu^k_\alpha(ns)\,T^\beta_k(sm)}{\Omega_{ms}-\omega_k}\right\} +$$

$$+\sum_k \varepsilon_{\alpha\beta\delta}\left\{\frac{B_\beta(ns)\,\mu^e_\delta(sm)}{\Omega_{ns}} - \frac{\mu^e_\delta(ns)\,B_\beta(sm)}{\Omega_{ms}}\right\}, \tag{14}$$

where

$$\tilde{\Phi}_i(ns) = \langle n | \phi_i(\rho) + B^{\rho\rho}_i J^2_\sigma | s\rangle,$$

$$T^\beta_k(ns) = \langle n | B^{\rho\rho}_k(\rho)J_\rho + \frac{1}{2}(J_\rho B^{\rho\rho}_k(\rho)) | s\rangle, \text{ and } J_\rho = -i\frac{\partial}{\partial\rho}.$$

The symbol $\Sigma*$ denotes the fact that terms with resonance denominators (i.e., with $\omega_i \approx \Omega_{ps}$) are removed from the sum. In the case of random resonances of the Fermi type ($\omega_1 \approx \Omega_{mn}$) or of the second Coriolis kind ($\omega_3 \approx \Omega_{mn}$) one has to make the change of variables in formulas (13) and (14)

$$\frac{\tilde{\Phi}_1(mn)\,\mu^1_\alpha(m)}{\Omega_{mn}-\omega_1} \to \frac{\tilde{\Phi}_1(mn)\,\mu^1_\alpha(m)}{\Omega_{mn}+\omega_1},$$

$$\frac{T^\beta_3(mn)\,\mu^3_\alpha(m)}{\Omega_{mn}-\omega_3} \to \frac{T^\beta_3(mn)\,\mu^3_\alpha(m)}{\Omega_{mn}+\omega_3}. \tag{15}$$

## AN EFFECTIVE DIPOLE MOMENT OF A MOLECULE FOR COMBINATION BANDS

The sought—after—matrix element

$\tilde{\mu}_Z(n, v_\kappa; v_\kappa + 1, m) = \langle n v_\kappa \,|\, \tilde{\mu}_Z \,|\, v_\kappa + 1, m\rangle$ can be reduced, as in the model of semirigid molecule, to the form

$$\tilde{\mu}_Z(n, v_k; v_k + 1, m) = \left(\frac{v_k + 1}{2}\right)^{1/2} \times$$
$$\times \left[\sum_{\alpha} \varphi_\alpha \tilde{\mu}^k_\alpha(nm) - i \sum_{\alpha\beta} \frac{1}{2}\{\varphi_\alpha, J_\beta\}\, {}^{\alpha,\beta}\tilde{M}_k(nm)\right], \qquad (16)$$

where

$$\tilde{\mu}^k_\alpha(nm) = \mu^k_\alpha(nm) + \frac{1}{2}\sum_s \left\{\frac{\tilde{\Phi}_{kk}(ns)\,\mu^k_\alpha(sm)}{\Omega_{ns}}\left(v_k + \frac{1}{2}\right) + \right.$$
$$\left. + \frac{\mu^k_\alpha(ns)\,\tilde{\Phi}_{kk}(sm)}{\Omega_{ms}}\left(v_k + \frac{3}{2}\right)\right\} + \sum_i \frac{\phi_{ik}(nm)\,\mu^k_\alpha(n)}{(\Omega_{mn} + \omega_i)^2 - \omega_k^2} +$$
$$+ \sum_s{}^{*} \left\{\frac{\tilde{\Phi}_k(ns)\,\mu^e_\alpha(sm)}{\Omega_{ns} - \omega_k} + \frac{\mu^e_\alpha(ns)\,\tilde{\Phi}_k(sm)}{\Omega_{ms} + \omega_k}\right\} -$$
$$- i \sum_s{}^{*} \sum_{\beta\gamma} \varepsilon_{\alpha\beta\delta}\left\{\frac{T^\beta_k(ns)\,\mu^e_\alpha(sm)}{\Omega_{ns} - \omega_k} + \frac{\mu^e_\alpha(ns)\,T^\beta_k(sm)}{\Omega_{ms} - \omega_k}\right\}; \qquad (17)$$

$${}^{\alpha,\beta}\tilde{M}_k(nm) = 2i \sum_s{}^{*} \left\{\frac{T^\beta_k(ns)\,\mu^e_\alpha(sm)}{\Omega_{ns} - \omega_k} - \frac{\mu^e_\alpha(ns)\,T^\beta_k(sm)}{\Omega_{sm} - \omega_k}\right\} +$$
$$+ \sum_s{}^{*} \sum_{\gamma\delta} \varepsilon_{\alpha\gamma\delta}\left\{\frac{B^{\gamma\delta}_k(ns)\,\mu^e_\delta(sm)}{\Omega_{ns} + \omega_k} + \frac{\mu^e_\delta(ns)\,B^{\gamma\delta}_k(sm)}{\Omega_{sm} + \omega_k}\right\} -$$
$$- 4 \sum_{j \neq k} (\omega_j \omega_k)^{-1/2} \frac{B_\beta(n)\,\zeta^\beta_{jk}(n)\,\mu^k_\alpha(nm)}{\omega_j^2 - \omega_k^2}. \qquad (18)$$

The Coriolis resonance of the first kind ($\omega_1 \approx \omega_3$) can be taken into account in formula (18) in the same way as in Ref. 9. The most significant difference from the model of semirigid molecule appears in the formulas for matrix elements that describe the relations between the states with different values of the quantum number $n$. At the same time, if the effective dipole moment describes the relations between the states with one and the same quantum number $n$, the sought-after formulas differ but slightly from similar relations of the model of semirigid molecule and therefore we shall not discuss them below. By way of example we present an expression for the effective dipole moment in the case of combination (difference) bands with $n = m$.

## AN EFFECTIVE DIPOLE MOMENT OF A MOLECULE IN THE CASE OF COMBINATION (DIFFERENCE) BANDS WITH $n = m$

The sought–after–matrix element is given in the form

$$\tilde{\mu}_Z(n, v_k, v_l; v_k + 1, v_l \pm 1, n) =$$
$$= \langle v_k, v_l, n \,|\, \tilde{\mu}_z \,|\, n, v_k + 1, v_l \pm 1\rangle = \left(\frac{v_k + 1}{2}\right)^{1/2} L_l(\pm) \times$$
$$\times \sum_\alpha \frac{1}{2}\varphi_\alpha \left\{\mu^{kl}_\alpha(n) + 4 \sum_s \frac{\phi_{kl}(ns)\,\mu^e_\alpha(ns)\,\Omega_{ns}}{\Omega_{ns}^2 - (\omega_k \pm \omega_l)^2} + \right.$$
$$\left. + 2 \sum_{\beta\gamma} \varepsilon_{\alpha\beta\gamma} \frac{B_\beta(n)\,\zeta^\beta_{kl}(n)\,\mu^e_\gamma(n)(\omega_k \pm \omega_l)}{(\omega_k \omega_l)^{1/2}(\omega_k \pm \omega_l)}\right\} + \ldots$$

The function $L_l(+) = \left(\frac{v_l + 1}{2}\right)^{1/2}$ for $v_l + 1$, and $L_l(-) = \left(\frac{v_l}{2}\right)^{1/2}$ for $v_l - 1$. This formula differs from the analogous[9] by the second term and by the fact that the diagonal matrix elements of the functions $\zeta(\rho)$, $B(\rho)$, and the like, are used in it instead of constants $\zeta$, $B$, ... . In the limiting case (see Eqs. (10) and (11)) $\tilde{\mu}_Z(n, v_\kappa, \ldots)$ is reduced to the function obtained in Ref. 9.

## APPLICATION TO H$_2$O MOLECULE

The above relations have been used for seeking for functions $\mu_x(\rho)$, $\overset{1}{\mu}_x(\rho)$, and $\overset{3}{\mu}_x(\rho)$ for the H$_2$O molecule based on relation (3). In doing this, we used experimental data on the coefficients $\tilde{\mu}_j \equiv \{\tilde{\mu}_\alpha, \mu_{\alpha,\beta}\}$, $j = 1, 2, \ldots M$ of the series expansion

$$\tilde{\mu}_Z = \tilde{\mu}_z \varphi_z + \tilde{\mu}_{x,y}\{\varphi_x, iJ_y\} + \tilde{\mu}_{y,x}\{i\varphi_y, J_x\} + \ldots,$$
$$\tilde{\mu}_Z = \tilde{\mu}_x \varphi_x + \tilde{\mu}_{y,z}\{i\varphi_y, J_z\} + \tilde{\mu}_{z,y}\{\varphi_z, iJ_y\} + \ldots, \qquad (19)$$

which are normally used in processing the experimental data on the bands of $A$ (odd $\Delta v_3$) or $B$ (even $\Delta v_3$), respectively. It is obvious that formulas (12) and (13) can easily be reduced to the form (19). The functions $\overset{e}{\mu}_x(\rho)$ and $\overset{i}{\mu}_\alpha(\rho)$ ($i = 1$ at $\alpha = \xi$ and $i = 3$ at $\alpha = z$) have been chosen in the form

$$\mu^\sigma_x(\rho) = a_1 \sin(\rho/2) + a_2 \sin^2(\rho/2) + a_3 \sin^3(\rho/2), \qquad (20)$$

$$\mu^\sigma_x(\rho) = a_{+2} \cos^2[(\pi - \rho)p] + a_{-2} \cos^2[(\pi - \rho)p] - C, \qquad (20a)$$

$$\mu^\sigma_z(\rho) = b_1 \cos(\rho/2) + b_2 \cos^2(\rho/2) + b_3 \cos^3(\rho/2), \qquad (20b)$$

where $\sigma$ takes the indices $e$ or $l$. When choosing the representation of the functions under consideration we assumed that for linear configuration of a molecule the following conditions should be satisfied:

$$\overset{e}{\mu}_x(\rho = 0)\,,\ \overset{1}{\mu}_x(\rho = 0) = 0. \qquad (21)$$

Under these conditions the constant $C$ entering into Eq. (20a) can be found from Eq. (21). The parameters $a$, $b$, $p$ are assumed to be variable and are found by minimizing the functional

$$S = \sum_{j=1}^{M}\left[(\tilde{\mu}_j^{\exp} - \tilde{\mu}_j^{calc})W_j\right]^2, \qquad (22)$$

where $W_j$ is the weight introduced so that the order of magnitude of all data used in the fitting procedure be one and the same. The wave functions $\Psi_n(\rho)$ from the matrix elements were determined by integrating numerically Eq. (9) in which the potential function $V_0(\rho)$ is given by

$$V_0(\rho) = f_{\alpha\alpha}\rho^2 + \frac{H[1 + f_{\alpha\alpha} \cdot \rho_e^2 / H]^2}{[1 + H\rho^2 / f_{\alpha\alpha} \cdot \rho_e^4]}$$

with the parameters $f_{\alpha\alpha} = 12857.902\ \text{cm}^{-1}$, $H = 10960.976\ \text{cm}^{-1}$, and $\rho_e = 1.8208$ rad. Integration of Eq. (4) was performed by the Numerov–Cooley[15] method. The functions $B_\alpha(\rho)$, $B_{\kappa}^{\alpha\beta}(\rho)$, ... can be taken from Refs. 8 and 13. The functions $\phi_i(\rho)$, $\omega_i(\rho)$, ... entering into the series expansion of a molecular potential were calculated using the technique described in Refs. 10 and 16 with the strength parameters $f_{ij}$, $f_{ijl}$ taken from Ref. 16.

*TABLE I. Calculated and experimentally measured parameters $\tilde{\mu}_x$, $\tilde{\mu}_{yz}$, and $\tilde{\mu}_{zy}(B, D)$ of the effective dipole moment of the* $H_2O$ *molecule, coupling the states $|n>$ and $|n + \Delta n>$ ($\nu_1 = \nu_3 = 0$).*

| $n$ | $\tilde{\mu}_x$ | $\tilde{\mu}_{yz}$ | $\tilde{\mu}_{zy}$ | $\tilde{\mu}_x$ | $\tilde{\mu}_{yz}$ | $\tilde{\mu}_{zy}$ |
|---|---|---|---|---|---|---|
| | $\Delta n = 0$ | | | $\Delta n = 1$ | | |
| 0 | −1.85 | | | 1.27E−01 | −6.5E−03 | −3.6E−04 |
| | (Ref. 1) | | | (Ref. 3) | | |
| 0 | −1.86 | | | 1.20E−01 | −7.3E−03 | −2.6E−04 |
| 1 | −1.83 | | | 1.82E−01 | −0.9E−02 | |
| | (Ref. 2) | | | (Ref. 6) | | |
| 1 | −1.83 | | | 1.77E−01 | −1.2E−02 | −3.4E−04 |
| 2 | −1.79 | | | 2.26E−01 | −1.8E−02 | −3.9E−04 |
| 3 | −1.75 | | | 2.75E−01 | −2.7E−02 | −4.2E−04 |
| 4 | −1.69 | | | 3.27E−01 | −4.5E−02 | −4.4E−04 |
| 5 | −1.61 | | | 3.90E−01 | −9.7E−02 | −4.4E−04 |
| 6 | −1.50 | | | 4.63E−01 | −2.8E−01 | −3.4E−04 |
| 7 | −1.39 | | | 5.15E−01 | −6.1E−01 | −4.1E−04 |
| | $\Delta n = 2$ | | | $\Delta n = 3$ | | |
| 0 | 5.82E−03 | −0.4E−04 | 2.3E−05 | 3.52E−04 | 1.1E−05 | 3.2E−05 |
| | (Ref. 4) | | | (Ref. 5) | | |
| 0 | 6.02E−03 | −1.8E−04 | 2.0E−05 | 3.23E−04 | 1.6E−05 | 3.2E−05 |
| 1 | 1.05E−02 | −3.0E−04 | 3.5E−05 | 4.12E−04 | 5.9E−05 | 6.2E−05 |
| 2 | 1.46E−02 | −3.5E−04 | 5.3E−05 | 7.29E−05 | 1.9E−04 | 9.3E−05 |
| 3 | 1.77E−02 | −5.5E−05 | 7.8E−05 | −1.33E−03 | 7.3E−04 | 1.3E−04 |
| 4 | 1.79E−02 | 2.3E−03 | 1.2E−04 | −6.32E−03 | 2.7E−03 | −1.8E−04 |
| 5 | 1.35E−02 | 1.3E−02 | 1.1E−04 | −1.38E−03 | 5.6E−03 | 3.3E−05 |
| | $\Delta n = 4$ | | | $\Delta n = 5$ | | |
| 0 | 4.9E−05 | | 1.2E−05 | −4.0E−05[a] | 6.0E−07 | 5.0E−07 |
| | (Ref. 7) | | | | | |
| 0 | −4.0E−05 | 7.1E−06 | −1.1E−05 | −1.2E−05[b] | −4.0E−07 | 7.0E−07 |
| 1 | −1.6E−04 | 2.4E−05 | −2.6E−05 | 4.0E−06[c] | 3.0E−07 | −1.0E−06 |
| 2 | −4.3E−04 | 7.2E−05 | −4.3E−05 | | | |
| 3 | −8.8E−04 | 1.6E−04 | −1.3E−04 | | | |

a) Calculations were made using (–) sign at the parameters $\tilde{\mu}_j$ of the band $4\nu_2$ and functions (20) and (20b).

b) Calculations were made using (–) sign at the parameters $\tilde{\mu}_j$ of the bands $3\nu_2$ and $4\nu_2$ and functions (20) and (20b).

c) Calculations were made using functions (20a) and (20b).

Results of calculations of the coefficients of the series expansion (19) are presented in Tables I–III together with the experimental data. For the case $\Delta_n = 0$ the values of matrix elements were calculated by formula (13). Total number of experimental values $M = 21$. The values of parameters $a$ and $b$ reconstructed by solving the inverse problem are given in Table IV, and the reconstructed function $\mu_x^e(\rho)$ is shown in the figure.

*TABLE II. Calculated and experimentally measured parameters $\tilde{\mu}_x$, $\tilde{\mu}_{yz}$, $\tilde{\mu}_{zy}(B, D)$ of the effective dipole moment of the* $H_2O$ *molecule, coupling the states $|n, \nu_1 = 0>$ and $|n + \Delta n, \nu_1 + 1>$ ($\nu_3 = 0$).*

| $n$ | $\tilde{\mu}_x$ | $\tilde{\mu}_{yz}$ | $\tilde{\mu}_{zy}$ | $\tilde{\mu}_x$ | $\tilde{\mu}_{yz}$ | $\tilde{\mu}_{zy}$ |
|---|---|---|---|---|---|---|
| | $\Delta n = 0$ | | | $\Delta n = 1$ | | |
| 0 | −1.5E−02 | 1.4E−03 | | | | |
| | Ref. (4) | | | | | |
| 0 | −1.5E−02 | 1.5E−03 | −5.0E−04 | | | |
| 1 | | | | 4.5E−03 | −2.5E−04 | |
| | | | | (Ref. 6) | | |
| 1 | −1.8E−02 | 1.7E−03 | −4.9E−04 | 4.5E−03 | −5.1E−05 | 1.0E−04 |
| 2 | −2.0E−02 | 1.9E−03 | −4.8E−04 | 6.0E−03 | −7.9E−05 | 1.4E−04 |
| 3 | −2.2E−02 | 2.2E−03 | −4.7E−04 | 6.7E−03 | −1.1E−04 | 1.8E−04 |
| 4 | | | | 6.8E−03 | −1.6E−04 | 2.1E−04 |
| | $\Delta n = +2$ | | | $\Delta n = -2$ | | |
| 0 | −2.10E−03 | −3.9E−06 | 1.0E−05 | −1.6E−03 | −7.0E−06 | −7.3E−06 |
| 1 | −3.50E−03 | −1.4E−05 | 1.9E−05 | −2.7E−03 | −7.8E−06 | −1.4E−05 |
| 2 | −4.50E−03 | −4.1E−05 | 2.9E−05 | −3.7E−03 | −2.5E−06 | −2.1E−05 |

*TABLE III. Calculated and experimentally measured parameters $\tilde{\mu}_z$, $\tilde{\mu}_{xy}$, $\tilde{\mu}_{yx}(B, D)$ of the effective dipole moment of the* $H_2O$ *molecule, coupling the states $|n, \nu_3 = 0>$ and $|n + \Delta n, \nu_3 = 1>$ ($\nu_1 = 0$).*

| $n$ | $\tilde{\mu}_x$ | $\tilde{\mu}_{yz}$ | $\tilde{\mu}_{zy}$ | $\tilde{\mu}_x$ | $\tilde{\mu}_{yz}$ | $\tilde{\mu}_{zy}$ |
|---|---|---|---|---|---|---|
| | $\Delta n = 0$ | | | $\Delta n = -1$ | | |
| 0 | 6.9E−02 | −6.5E−04 | 1.7E−03 | | | |
| | (Ref. 4) | | | | | |
| 0 | 7.0E−02 | −2.1E−06 | 8.4E−04 | | | |
| 1 | 6.5E−02 | −3.5E−06 | 8.5E−04 | 2.3E−02 | −7.2E−06 | −5.6E−05 |
| 2 | 6.0E−02 | −5.3E−06 | 8.7E−04 | 3.1E−02 | −1.1E−05 | −8.6E−05 |
| 3 | 5.5E−02 | −8.3E−06 | 9.0E−04 | 3.6E−02 | −1.5E−05 | −1.2E−04 |
| 4 | | | | 3.8E−02 | −1.9E−05 | −1.5E−04 |

*TABLE IV. Parameters of model representations of the functions $\mu_x^\sigma(\rho)$ ($\sigma = e, 1$) and $\mu_z^3(\rho)(B, D)$ of the* $H_2O$ *molecule.*

| | $\mu_x^e$ | $\mu_x^1$ | | $\mu_z^3$ |
|---|---|---|---|---|
| $a_1$ | −4.9511 | −0.3350 | $b_1$ | −1.3437 |
| $a_2$ | 4.3364 | 1.0082 | $b_2$ | 3.6678 |
| $a_3$ | −2.0080 | −0.8401 | $b_3$ | −2.28005 |
| $a_{+2}$ | 0.3525 | 0.1828 | $b_1$ | 2.200 |
| $a_{-2}$ | 0.3532 | 0.1079 | $b_2$ | −5.3047 |
| $p$ | −1.4491 | −0.0719 | $b_3$ | 3.3767 |

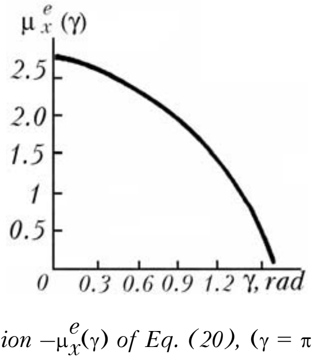

*FIG. 1. Function $-\mu_x^e(\gamma)$ of Eq. (20), ($\gamma = \pi - \rho$) obtained for the* $H_2O$ *molecule by minimizing functional (22).*

## CONCLUSION

First we should like to make some remarks concerning the choice of a sign of the parameters $\tilde{\mu}_j^{\exp}$. Inverse problems for the bands $3\nu_2$ and $4\nu_2$ have been solved using opposite signs of the parameters $\tilde{\mu}_j^{\exp}$. Thus the calculational data (a) presented in Table I were obtained with (–) sign of the $\tilde{\mu}_j^{\exp}$ to $4\nu_2$ band. The calculational data (b) from this table also used (–) sign of the $\tilde{\mu}_j^{\exp}$ parameter in the bands $3\nu_2$ and $4\nu_2$, and functions (20a) and (20b). The (–) signs of the $\tilde{\mu}_j^{\exp}$, is preferable in the case of $4\nu_2$ band if model representations (20a) and (20b) are used, since these functions with the parameters obtained from experimental data for bands $\nu_2$, $2\nu_2$, and $3\nu_2$ and for the ground state result, in direct calculations, in (–) $\tilde{\mu}_j^{\text{calc}}$ signs for the band $4\nu_2$.

Experimental data are described most adequately (i.e., without changing sign of $\tilde{\mu}_j^{\exp}$) by the function of the Eq. (20a) type in which the power 2 should be replaced by 4. However, the accuracy of reconstruction made using functions (20) and (20b) is higher. Note once more that the proposed here functions (20) are the model functions and the parameters $a$ and $b$ from Table IV are optimal in the sense of Eq. (19), i.e., they describe the set of experimental data on $\tilde{\mu}_j^{\exp}$ best of all. Nevertheless these functions enable one to calculate the parameters $\tilde{\mu}_j^{\exp}$ (see Tables I – III) for a number of bands, for which experimental data on intensities are unvailable.

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