Calculating parameters of the H₂S molecule dipole moment function

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Based on the formalism of effective dipole moment operators, analytical equations have been derived for a twice-transformed dipole moment. Complete equations for the transformed vibrational moments of the transitions with $\Delta V \leq 3$ have been obtained in terms of molecular parameters. A set of linear equations describing the evaluation of the dipole moment function derivatives has been derived. Based on the experimental data on the transition moment operators, derivatives up to the third order have been calculated for the H₂S molecule. The proposed scheme for estimation of the derivatives can be used for all types of molecules. It provides for explanation of the discrepancy between the calculated first derivatives of the dipole moment function and the *ab initio* results for the H₂S molecule.

Introduction

Knowledge of the spectrum of sulfurous anhydride H₂S and its peculiarities is of great importance, first of all, for understanding chemical processes in the atmospheres of giant planets, such as Jupiter, as well as in evaluating industrial and volcanic emissions.

One of the features of this molecule is weak intensity of fundamental bands.[1] They are much weaker than the intensity of the same bands for H₂O (Ref. 2) and H₂Se molecules (Ref. 3). One more feature is the anomalous distribution of intensity over branches and its dependence on the difference of the rotational quantum numbers K (Ref. 4).

It is known that the intensity of lines is proportional to squared matrix element of the dipole moment operator of a molecule. Thus, we can assume that the dipole moment function of the H₂S molecule has some characteristics that make it distinguishable from other asymmetric-top molecules, such as O₃ (Ref. 5) and H₂O (Refs. 2 and 6). This is also confirmed by the fact that calculated results on the first derivatives of the dipole moment function with respect to normal coordinates as obtained from empirical values of the transition moments[2] differ significantly from the results of *ab initio* calculations.[7,22,23] At the same time, the second derivatives[7] exceed the first derivatives, thus breaking the linear approximation of the dipole moment function, and higher derivatives play an important role in construction of the model function.

In this connection, we have formulated the task, based on our experience in calculating the dipole moment functions of the asymmetric-top molecules by the method of effective operators,[5] to correctly calculate parameters of the dipole moment function of the H₂S molecule with the account for the above features. In constructing the model, we used the formalism developed in Ref. 5, and all data available on the transition moments of the vibrational bands with $\Delta V \leq 3$ were used in the calculations.

Theory

It is well-known that the intensity of transition from the rotational-vibrational state a to the state b is proportional to the squared matrix element of the dipole moment:

$$S_{ab} = |\langle \Psi_a | \mu_Z | \Psi_b \rangle|^2, \tag{1}$$

where Ψ_a and Ψ_b are wave functions of the corresponding states; μ_Z is the projection of dipole moment in the space-fixed coordinate system; it can be expressed through projections in the molecule-fixed system $^\alpha\mu$ and directional cosines $\varphi_{Z\alpha} \equiv \varphi_\alpha$.

$$\mu_Z = \sum_\alpha \varphi_{Z\alpha} \, ^\alpha\mu. \tag{2}$$

The projection of the dipole moment $^\alpha\mu$ in the molecule-fixed system is usually presented by a series over normal coordinates:

$$^\alpha\mu = {}^\alpha\mu_e + \sum_k {}^\alpha\mu_k \, q_k + \sum_{k \leq l} {}^\alpha\mu_{kl} \, q_k \, q_l +$$
$$+ \sum_{k \leq l \leq m} {}^\alpha\mu_{klm} \, q_k \, q_l \, q_m + \dots . \tag{3}$$

The coefficients of expansion $^\alpha\mu_k$, $^\alpha\mu_{kl}$, and $^\alpha\mu_{klm}$ are (accurate to $1/n!$ factors) derivatives of the dipole moment function of the molecule (see Ref. 2 and Appendix 1 in Ref. 5). These derivatives, in their turn, can be found from solution of the inverse spectroscopic problem for line intensities or from *ab initio* calculations. Various theoretical approaches and methods are used for calculation of line intensities.

In this paper, we use the formalism of the effective Hamiltonian operators and dipole moment.[2,8] Using the

perturbation theory within the framework of this approach, we can relate parameters of the effective transition moments determined from processing the experimental data with the dipole moment function.

The operator of the effective dipole moment $\tilde{\mu}_Z$ is connected with the projection of the dipole moment μ_Z by the same unitary transformations that are applied to the rotational-vibrational molecular Hamiltonian H at derivation of the effective Hamiltonians:

$$\tilde{\mu}_Z = \dots e^{iS_2} e^{iS_1} \mu_Z e^{-iS_1} e^{-iS_2} . \quad (4)$$

Here the transformation operators like generators S_1, S_2, etc. are functions of the projections of the total angular momentum J_α and rotational operators.[2,8,9] The use of designations proposed in Ref. 8 allows us to write $\tilde{\mu}_Z$ in the form:

$$\tilde{\mu}_Z = \sum_{m,n} \tilde{M}_{mn} , \ \tilde{M}_{mn} \sim r^m J^{n-1} \varphi , \quad (5)$$

where the index m is for the total vibrational power of the operator, and n is for the total rotational power.

Thus, the operator of effective dipole moment is a series expansion over both vibrational and rotational operators. To separate of the operator of effective dipole moment by orders of magnitude, it is convenient to use the Amat–Nielsen scheme, in which terms $\tilde{M}_{mn}$ are, on the average, of the order of $\lambda^{m+n-1}(^\alpha\mu_e)$. In such an approach, individual operators $\tilde{M}_{mn}$ can correspond to the probabilities of certain rotational-vibrational transitions. Thus, the $\tilde{M}_{11}$ operator describes the transitions that make up fundamental bands, and the operators $\tilde{M}_{21}$ and $\tilde{M}_{31}$ describe, respectively, the transitions of the first and second overtones and combination bands. The explicit equations for the operators $\tilde{M}_{mn}$ with low values of $m + n$ are rather well known.[2,8]

This scheme allows us to find independently the first derivatives of the dipole moment function, then the second derivatives, then the third ones, and so on with the use of perturbation theory and data on the vibrational transition moments.[2,5] However, for the H$_2$S molecule the dipole moment function has the peculiarity of low values of the first derivatives. This peculiarity distorts the ordinary expansion by orders of smallness and requires the terms of higher orders of perturbation theory to be taken into account at calculation of one-quantum transitions.

In this case, the effective dipole moment operators including the rotational operator in the first power ($n = 1$) for the considered transitions can be written as follows:

$$\Sigma \Delta v_i = 1, \ (\tilde{\mu}_Z)_{(n=1)} = \tilde{M}_{11} + \tilde{M}'_{31} + \dots,$$

$$\Sigma \Delta v_i = 2, \ (\tilde{\mu}_Z)_{(n=1)} = \tilde{M}_{21} + \dots, \quad (6)$$

$$\Sigma \Delta v_i = 3, \ (\tilde{\mu}_Z)_{(n=1)} = \tilde{M}_{31} + \dots .$$

Since we construct the dipole moment function up to the third derivatives, let us consider, as in our previous paper,[5] the double transformed dipole moment operator (it is sufficient for vibrational transitions with $\Delta V \leq 3$). The allowance made for the terms of the third order of perturbation theory $\tilde{M}'_{31}$ for description of probabilities of vibrational transitions with $\Delta v_i = 1$ leads to a set of interconnected equations (6), which should be solved to determine the parameters of the dipole moment function.

For more convenient consideration, separate the directional cosines from the operators $\tilde{M}_{m1}$:

$$\tilde{M}_{mn} = 1/2 \sum_\beta \{^\alpha \tilde{\mu}_{mn-1}, \varphi_\alpha\}. \quad (7)$$

The use of the method of contact transformations and the representation of secondary quantization with the vibrational birth a_n^+ and annihilation a_l operators and with the technique of normal ordering described in Ref. 9 allows us to write the explicit form of the operators $^\alpha\tilde{\mu}_{m0}$ with $m = 1, 2, 3$

$m = 1$:

$$^\alpha\tilde{\mu}_{10} = \sum_i \{\Gamma_i^\alpha + \sum_j G_{ij}^\alpha a_j^+ a_j\}(a_i^+ + a_i) \quad (8a)$$

$m = 2$:

$$^\alpha\tilde{\mu}_{20} = \sum_{i,j} [\Gamma_{ij}^\alpha (a_i^+ a_j^+ + a_i a_j) + Q_{ij}^\alpha (a_i^+ a_j + a_j^+ a_i)] \quad (8b)$$

$m = 3$:

$$^\alpha\tilde{\mu}_{30} = \sum_{i,j,l} [\Gamma_{ijl}^\alpha (a_i^+ a_j^+ a_l^+ + a_i a_j a_l) +$$
$$+ Q_{ijl}^\alpha (a_i^+ a_j^+ a_l + a_l^+ a_i a_j)]. \quad (8c)$$

It should be noted that the coefficients Γ_i^α are the corresponding first derivatives of the dipole moment function multiplied by $1/\sqrt{2}$ (Ref. 2) in the case that the consideration is restricted to the first order of smallness for one-quantum transitions. The equations for the coefficients Γ_i^α with allowance for the terms of the third order of smallness are complex functions depending on the first, second, and third derivatives of the dipole moment function, as well as the parameters of the molecular potential function, and they are presented in this paper for the first time

$$\Gamma_i^\alpha = g_0^i(^\alpha\mu_e) + g_1^i(^\alpha\mu_k) + g_2^i(^\alpha\mu_{kl}) + g_3^i(^\alpha\mu_{klm}) + \dots . \quad (9)$$

The complex dependence of the coefficients Γ_i^α on the derivatives [Eq. (9)] indicates that the first derivatives of the dipole moment function cannot be found independently based only on the information on the vibrational transition moments of fundamental bands, as it was done in Ref. 2. To construct the dipole moment function, we should use all the information on the transition moments with $\Delta V \leq 3$ and solve the set of linear equations. The equations for the coefficients

Γ_{ij}^{α} and Q_{ij}^{α} for two-quantum transitions $m = 2$ ($\Sigma\Delta v_i = 2$) are well-known[2,8,10]:

$$\Gamma_{ij}^{\alpha} = g_0^{ij}(^{\alpha}\mu_e) + g_1^{ij}(^{\alpha}\mu_k) + g_2^{ij}(^{\alpha}\mu_{kl}) + \dots . \quad (10)$$

In our previous paper,[5] we presented explicit equations for these coefficients Γ_{ijl}^{α} and Q_{ijl}^{α} in the case of three-quantum transitions $m = 3$ ($\Sigma\Delta v_i = 3$):

$$\Gamma_{ijl}^{\alpha} = g_0^{ijl}(^{\alpha}\mu_e) + g_1^{ijl}(^{\alpha}\mu_k) + g_2^{ijl}(^{\alpha}\mu_{kl}) + g_3^{ijl}(^{\alpha}\mu_{klm}) + \dots . (11)$$

Since in this work we do not use the data on the intensity of hot and difference transitions, we present the equations only for the coefficients Γ, separating the explicit dependences on the parameters of the dipole moment function in them. The values of the coefficient g are given in the Appendix 1. The superscripts of the coefficients g, as the subscripts of Γ, number the vibrational modes, and the indices 1, 2, and 3 denote the dependence on the first, second, and third derivatives, respectively.

It is well known that the method of effective dipole moment[2] significantly simplifies the calculation of the transition probabilities, replacing calculation of matrix elements of the molecular dipole moment (2) in exact wave functions

$$\langle \Psi_a | \mu_Z | \Psi_b \rangle = {}^{eff}\langle \Psi_a | \tilde{\mu}_Z | \Psi_b \rangle^{eff} \quad (12)$$

by calculating matrix elements of the transformed dipole moment in the effective wave functions

$$| \Psi \rangle^{eff} = | v_1 \, v_2 \, v_3 \, JK_a K_c \rangle^{eff} =$$
$$= \sum_{V \in \{P\}} | \mathbf{V} \rangle \sum_K C_{JK\gamma}^V | JK\gamma \rangle, \quad (13)$$

where $\mathbf{V}$ takes sequentially all values in a given polyad P. $| \mathbf{V} \rangle \equiv | v_1 \rangle | v_2 \rangle | v_3 \rangle$ are wave functions of the harmonic oscillator, $| JK\gamma \rangle$ are the symmetrized rotational wave functions, and the eigenvectors $C_{JK\gamma}^V$ are determined from diagonalization of the effective Hamiltonian matrix, i.e., from processing of either line positions or energy levels.

When processing intensities of individual bands $(v_1 \, v_2 \, v_3) \to (v_1' \, v_2' \, v_3')$, it is convenient to use the so-called effective operators of transition moment ${}^{VV'}\tilde{\mu}_Z$ determined in Refs. 2 and 11 by writing the transformed dipole moment in the form:

$$\tilde{\mu}_Z = \sum_{VV'} | \mathbf{V} \rangle {}^{VV'}\tilde{\mu}_Z \langle \mathbf{V'} |, \quad (14)$$

where

$${}^{VV'}\tilde{\mu}_Z = \langle \mathbf{V} | \tilde{\mu}_Z | \mathbf{V'} \rangle . \quad (15)$$

This procedure determines the transition moment operators as purely rotational operators depending on directional cosines φ_α and components of the angular momentum operator J_α. The vibrational transition moment includes only the corresponding directional cosine depending on the type of the vibrational band (type A or B). To find the explicit equations for the vibrational transition moments ${}^{VV'}\tilde{\mu}_Z$ of the bands under study [set of equations (8)], we have to calculate the known matrix elements of the birth and annihilation operators in the basis of wave functions of harmonic oscillator. Using the designations we have proposed in Refs. 5 and 9 and determining the vector of the upper vibrational state $\mathbf{V'}$ as $\mathbf{V'} = \mathbf{V} \pm \mathbf{1}_k \pm \mathbf{1}_l \pm \mathbf{1}_p$, the contributions coming from the vibrational moments to one-, two-, and three-quantum transitions can be written as follows:

$$\langle \mathbf{V} | {}^{\alpha}\tilde{\mu}_{10} | \mathbf{V} + \mathbf{1}_k \rangle = f^k(\mathbf{V}) \theta_\alpha^k ; \quad (16)$$

$$\langle \mathbf{V} | {}^{\alpha}\tilde{\mu}_{20} | \mathbf{V} + \mathbf{1}_k + \mathbf{1}_l \rangle = f^{kl}(\mathbf{V}) \theta_\alpha^{kl} ; \quad (17)$$

$$\langle \mathbf{V} | {}^{\alpha}\tilde{\mu}_{30} | \mathbf{V} + \mathbf{1}_k + \mathbf{1}_l + \mathbf{1}_p \rangle = f^{klp}(\mathbf{V}) \theta_\alpha^{klp}. \quad (18)$$

The coefficients θ_α at the vibrational transition moments are rather simply related to the coefficients Γ^α and Q^α of the transformed dipole moment. Thus, $\theta_\alpha^k = \Gamma_k^\alpha$, $\theta_\alpha^{kk} = \Gamma_{kk}^\alpha$, $\theta_\alpha^{kp} = \Gamma_{pk}^\alpha$, $f(\mathbf{V})$ are the functions of vibrational quantum numbers and the equations for them are well known.[2,5,8,9] The rest equations are given in Table 1 (Ref. 5).

Thus, thanks to the method of contact transformations, we can express the parameters θ_α as functions of molecular parameters, anharmonicity constants K_{ijl}, K_{ijlm}, components of the constant dipole moment ${}^{\alpha}\mu_e$, and derivatives of the dipole moment function ${}^{\alpha}\mu_k$, ${}^{\alpha}\mu_{kl}$, ${}^{\alpha}\mu_{klm}$.

Calculation of derivatives of the dipole moment function

It is known that for the asymmetric-top molecule, if the consideration is restricted to the third order of smallness, the dipole moment function has 19 unknown derivatives, and to determine them, we need a set of at least 19 equations. Above we have constructed such a set: equations (16)−(18). The known values in this set are empiric parameters of models used for processing of intensities. As was already noted, at processing of intensities the transition moment operators are written as a series over rotational operators[2,11]:

$${}^{VV'}\tilde{\mu}_Z = \langle \mathbf{V} | \tilde{\mu}_Z | \mathbf{V'} \rangle =$$

$$= \left[\sum_\alpha {}^{VV'}T_\alpha \varphi_\alpha - i / 2 \sum_{\alpha,\beta} {}^{VV'}T_{\alpha,\beta} \{\varphi_\alpha, J_\beta\} + \right.$$

$$\left. + 1 / 2 \sum_{\alpha,\beta,\gamma} {}^{VV'}T_{\alpha,\beta\gamma} \{\varphi_\alpha, J_\beta J_\gamma\} + \dots \right]. \quad (19)$$

The explicit form of rotational operators entering into Eq. (19) depends on the type of a vibrational band: A or B. At simulation, the consideration is usually restricted to eight terms of the series, the parameters $\{{}^{VV'}T\}$ are declared empirical and determined from

processing of intensities by the least squares method. In this paper, we use the same designations for the empirical parameters $\{^{VV'}T\}$ as in Ref. 5, though those differ from the generally accepted ones.[11]

Of the entire series of empirical parameters $\{^{VV'}T\}$, the parameters $^{VV'}T_\alpha$, corresponding to the operators $^\alpha\tilde\mu_{m0}$ (8) in the transformed dipole moment, make the largest contributions. These parameters $^{VV'}T_\alpha$ for 19 vibrational bands that are given in Table 1 were taken for determination of the derivatives of the dipole moment function of H_2S molecule.

Table 1. Parameters of the vibrational transition moments $\{^{VV'}T_\alpha\}$*, used in calculations in this work

Polyad	Band	Value of parameter $^{VV'}T_\alpha \cdot 10^2$, D	Reference
1	ν_1	$(0.294_{94} \pm 0.002_1)$	4
	ν_3	$0.021_{37} \pm 0.001_4)$	
	$2\nu_2$	$(-0.346_2 \pm 0.010)$	
2	ν_2	$(-0.969_0 \pm 0.050)$	12
3	$\nu_1+\nu_2$	$0.683_{06} \pm 0.012$	13
	$3\nu_2$	$0.100_{06} \pm 0.030$	
	$\nu_2+\nu_3$	$887_{51} \pm 0.015$	
4	$\nu_1+\nu_3$	$(-0.311_6 \pm 0.050)$	14
	$2\nu_1$	$0.215_5 \pm 0.021$	
	$2\nu_3$	$0.090_2 \pm 0.026$	
	$\nu_1+2\nu_2$	$0.047_{85} \pm 0.001$	
	$2\nu_2+\nu_3$	$0.092_{41} \pm 0.002$	
5	$2\nu_1+\nu_2$	$0.083_{59} \pm 0.002$	15
	$\nu_1+\nu_2+\nu_3$	$0.191_{86} \pm 0.002$	
	$\nu_2+2\nu_3$	0.0	
6	$3\nu_1$	$(-0.026_{70} \pm 0.002)$	16
	$2\nu_1+\nu_3$	$0.048_{25} \pm 0.002$	
	$\nu_1+2\nu_3$	$0.019_{97} \pm 0.002$	
	$3\nu_3$	$(-0.020_{42} \pm 0.002)$	

* The designation $^{VV'}T_\alpha$ corresponds to the commonly accepted $^{VV''}\mu_1$.

Before coming to calculations, it should be noted that there exists a problem of ambiguity in the parameters of the effective dipole moment $\{^{VV'}T\}$ that were obtained by different authors from processing the experimental spectra. This ambiguity arises, because the unitary transformations that are applied to the operators do not change the operator form of the effective Hamiltonian or the effective dipole moment, but can significantly change the parameters

$$\tilde T = T + \Delta T.$$

Each set of the effective Hamiltonian parameters corresponds to a certain set of parameters of the effective dipole moment. Therefore, in comparing experimental values with the calculated data, we should use the corresponding models of the effective Hamiltonian and the effective dipole moment. All the experimental data on the transition moments given in Table 1 were obtained for the models of effective

Hamiltonians, in which the vibrational Fermi resonance was thought insignificant, and the effective value of the constant F was correspondingly assumed equal to zero. The same conditions were fulfilled when writing explicit equations for the transformed dipole moment.

As known, one of the important problems in calculation of derivatives is the problem of selecting the sign of the derivative. This problem arises because the line intensity is proportional to the squared matrix element of the dipole moment, which can have both positive (+) and negative (−) sign. The procedure of the method of least squares used at processing of experimental intensities allows determination of sign (+) or (−) for the parameters of interacting bands. Thus, there is an ambiguity in determination of the so-called common phase factor $(-1)^\varepsilon$ (Ref. 5) for polyads, which combine vibrational states in the presence of a resonance between them. Numeration of polyads used in this paper is given in Table 1.

Introduction of the phase factor allows us to relate the empirical parameters of transition moments $^{VV'}T_\alpha$ with their values found with the help of the perturbation theory as follows:

$$(-1)^\varepsilon \ (^{VV'}T_\alpha) = \{f(\mathbf{V})\theta_\alpha\}. \qquad (20)$$

The left-hand side of the equation presents the experimental values, and the right-hand side gives the relations for the parameters $\{\theta_\alpha\}$ containing the sought derivatives of the dipole moment (see Eqs. (9)−(11), (16)−(18), and Appendix 1). Now, having known the parameters of the potential function, values of the constant dipole moment and the inertia tensor of the molecule, we can find the derivatives of the dipole moment by solving the set of 19 linear equations. However, the difficulty is in the fact that the set has 2^6 solutions, i.e., 64 sets of derivatives. This is explained by the fact that the phase factor in the six selected polyads can be both +1 and −1, thus leading to different values and signs of the derivatives. How can we determine the correct solution?

To remove this ambiguity, in the generally accepted scheme, which involves sequential determination of first, second, and third derivatives, the signs are selected based on *ab initio* calculations, on the analysis of the so-called rotational corrections $^{VV'}T_{\alpha\beta}$ (19) and calculations for difference bands.[2,5,17] For the case of H_2S molecule in selecting the phase factors, we took, as the reference parameters, the values of the second derivatives found from empirical calculations that are in close agreement with the *ab initio* calculations.[23]

The agreement of the values of the second derivatives determined the phase factors of the 1st, 3rd, and 4th polyads as positive (+), and this allowed the number of solutions to be decreased down to 2^3. For the second polyad represented by only one state ν_2, we also took the positive (+) phase factor, and this determined the sign of the first derivative with respect to the second coordinate $^x\mu_2$ as negative. This all allowed the number of solutions of the system to be

decreased down to four. The four found sets of derivatives of the dipole moment function and their errors are presented in Table 2, along with the phase factors of the polyads, used in solving the set of equations. The absence of data on intensities of difference bands did not allow us to draw any final conclusion, as in Ref. 5, on the signs and values of the third derivatives.

Analysis of calculated results

Solving the set of equations (20), we succeeded in analyzing the contributions coming from each derivative to the corresponding parameter of transition moments for all of the 19 vibrational bands. The results of numerical calculation of the functions g for each derivative entering into Eqs. (9)−(11) in the case that the phase factor of all the polyads is positive are given in Table 3. The analysis of contributions is especially obvious for the fundamental bands.

As is seen from Table 3, the contributions including the second and third derivatives of the dipole moment function that arise when taking into account the third order of smallness of perturbation theory are comparable with the first derivatives and therefore they cannot be neglected. Neglect of the contributions of the third order leads to incorrect estimates of the first derivatives of the dipole moment function.[2]

It should be noted that the parameters of transition moments of the vibrational bands with $\Delta V = 2$ are almost independent of the first derivatives and they, on the whole, bear the information on the second derivatives. This allows us to estimate the second derivatives independently of the first and third ones. For the transitions with $\Delta V = 3$ the contributions of the coefficients including the second derivatives are large, whereas the contributions of the first derivatives are small and can be neglected.

Thus, numerical analysis of contributions to the parameters $^{VV'}T_\alpha$ of transition moments shows that for the moments of fundamental bands the contributions from the second and third derivatives of the dipole moment function are comparable with or even larger than the contribution from the first one. All the calculations were made with the parameters of the potential function taken from Ref. 18. To estimate the accuracy of the derivatives depending on the molecular potential function, we made the calculations for the four known sets of parameters of the potential function.[18–21] Here we did not present the results of these calculations, since the obtained values of the derivatives vary within the accuracy of Table 2. This also corresponds to the calculated results presented in Table 3, where for the transitions with $\Delta V = 2$ and $\Delta V = 3$ the functions g dependent on the first derivatives and parameters of the potential function are in practice negligibly small. The effect of cubic anharmonicity is marked only when estimating the contributions depending on the second derivatives.

Table 2. Parameters of the dipole moment function of the H$_2$S molecule calculated from the normal coordinates *, in D

Polyad	1 2 3 4 5 6	1 2 3 4 5 6	1 2 3 4 5 6	1 2 3 4 5 6	Error · 10^2
Phase factor $(-1)^\varepsilon$	+ + + + + +	+ + + + − +	+ + + + + −	+ + + + − −	
$^x\mu_1 \cdot 10^2$	0.160	0.155	0.110	0.110	0.07
$^x\mu_2 \cdot 10^2$	−2.11	−1.94	−2.11	−1.94	0.5
$^z\mu_3 \cdot 10^2$	0.30	0.30	0.33	0.33	0.05
$^x\mu_{11} \cdot 10^2$	0.32	0.32	0.31	0.31	0.04
$^x\mu_{12} \cdot 10^2$	1.39	1.38	1.39	1.38	0.02
$^x\mu_{22} \cdot 10^2$	−0.48	−0.48	−0.49	−0.49	0.01
$^z\mu_{13} \cdot 10^2$	−0.58	−0.58	−0.58	−0.58	0.01
$^z\mu_{23} \cdot 10^2$	1.57	1.57	1.57	1.57	0.01
$^x\mu_{33} \cdot 10^2$	0.14	0.14	0.14	0.14	0.04
$^x\mu_{111} \cdot 10^2$	0.010	0.010	0.070	0.070	0.003
$^x\mu_{112} \cdot 10^2$	0.24	−0.10	0.24	−0.10	0.04
$^x\mu_{122} \cdot 10^2$	0.16	0.16	0.16	0.16	0.01
$^x\mu_{222} \cdot 10^2$	0.24	0.24	0.24	0.24	0.02
$^z\mu_{113} \cdot 10^2$	−0.03	−0.03	−0.22	−0.22	0.01
$^z\mu_{123} \cdot 10^2$	0.73	−0.35	0.73	−0.35	0.07
$^z\mu_{223} \cdot 10^2$	0.10	0.10	0.10	0.10	0.05
$^x\mu_{133} \cdot 10^2$	0.11	0.11	0.03	0.03	0.01
$^x\mu_{233} \cdot 10^2$	0.08	0.08	0.08	0.08	0.03
$^z\mu_{333} \cdot 10^2$	−0.060	−0.060	−0.020	−0.020	0.005

* The harmonic frequencies and anharmonic constants used in calculations have first been recalculated based on the force fields given in Ref. 18.

**Table 3. Estimated contributions of the coefficients including the corresponding derivatives
of the dipole moment function to the parameters of vibrational transition moments for the H$_2$S molecule (D · 10^3)***

Vibrational band	α	$VV'T_\alpha$	${}^x\mu_e$	${}^x\mu_1$	${}^x\mu_2$	${}^z\mu_3$	${}^x\mu_{11}$	${}^x\mu_{12}$	${}^z\mu_{13}$	${}^x\mu_{22}$	${}^z\mu_{23}$	${}^x\mu_{33}$	${}^x\mu_{111}$	${}^x\mu_{112}$	${}^z\mu_{113}$	${}^x\mu_{122}$	${}^z\mu_{123}$	${}^x\mu_{133}$	${}^x\mu_{222}$	${}^z\mu_{223}$	${}^x\mu_{233}$	${}^z\mu_{333}$
ν_1	x	4.2		1.5	−0.0		1.6	−0.2		−0.4		0.2	0.1			0.8		0.6				
ν_2	x	−13.7		−0.0	−21.4	0.0	−0.0	2.4		0.1		−0.0		1.2					3.6		0.4	
ν_3	z	0.3	0.0	−0.0	0.1	3.0			−1.9		−0.4				−0.1					0.5		−1.0
$2\nu_1$	x	3.1		−0.1	−0.0		3.2															
$\nu_1+\nu_2$	x	13.7		0.0	−0.2			13.8														
$\nu_1+\nu_3$	z	−6.2	0.0			−0.4			−5.8													
$2\nu_2$	x	−4.9		−0.2	0.1					−4.8												
$\nu_2+\nu_3$	z	17.8	2.0			0.0					15.7											
$2\nu_3$	x	1.3		−0.1	−0.0							1.4										
$3\nu_1$	x	−0.3		0.0	0.0		−0.4	0.0					0.1									
$2\nu_1+\nu_2$	x	1.7		−0.0	0.0		0.1	−0.8		−0.0				2.4								
$2\nu_1+\nu_3$	z	1.0	−0.0			0.1			1.2		0.0				−0.3							
$\nu_1+2\nu_2$	x	1.0		0.0	−0.0			−0.6		0.1		−0.1				1.6						
$\nu_1+\nu_2+\nu_3$	z	5.4	0.2			−0.0			−0.2		−1.9					7.3						
$\nu_1+2\nu_3$	x	0.4		0.0	−0.0			−0.4		0.0		−0.4						1.1				
$3\nu_2$	x	1.2		−0.0	0.0			−1.3		0.0									2.4			
$2\nu_2+\nu_3$	z	1.9	0.0			0.0			0.6		0.2									1.0		
$\nu_2+2\nu_3$	x	~ 0		−0.0	0.1			−0.9		−0.0		0.1									0.8	
$3\nu_3$	z	−0.2	−0.0			0.0			0.4		0.0											−0.6

* The values are rounded to the first digit after the point (0.0 means that the value is less than 0.05). The empty cells mean that the corresponding derivatives, theoretically, do not contribute to the considered approximation. The force field was taken from Ref. 18.

Table 4. Comparison of the parameters of the dipole moment function of the H$_2$S molecule obtained by different methods, in D · 10^3

Parameter	This work*	Traditional scheme**	ab initio calculations		
			Set I [Ref. 7] (CEPA cal.)	Set II [Ref. 7] (SCF cal.)	Set III [Ref. 23] (CCSD [T])
${}^x\mu_1$	1.60	4.16 (Ref. 3)	6.8	1.90	1.63
${}^x\mu_2$	−21.1	−13.7 (Ref. 3)	−27.0	−32.2	−23.36
${}^z\mu_3$	3.00	0.30 (Ref. 3)	5.5	1.1	2.48
${}^x\mu_{11}$	3.20	3.20	8.2	5.6	3.64
${}^x\mu_{12}$	13.9	13.9	14.0	16.1	15.6
${}^x\mu_{22}$	−4.8	−4.8	−8.4	−11.2	−4.03
${}^z\mu_{13}$	−5.8	−5.8	−8.1	−7.2	−6.1
${}^z\mu_{23}$	15.7	15.7	16.6	19.5	17.35
${}^x\mu_{33}$	1.4	1.4	3.4	4.8	0.91
${}^x\mu_{111}$	0.10	–	–	–	–
${}^x\mu_{112}$	2.4	–	–	–	–
${}^x\mu_{122}$	1.6	–	–	–	–
${}^x\mu_{222}$	2.4	–	–	–	–
${}^z\mu_{113}$	−0.3	–	–	–	–
${}^z\mu_{123}$	7.3	–	–	–	–
${}^z\mu_{223}$	1.0	–	–	–	–
${}^x\mu_{133}$	1.1	–	–	–	–
${}^x\mu_{233}$	0.8	–	–	–	–
${}^z\mu_{333}$	−0.60	–	–	–	–

* For a comparison, we took the calculated results obtained with the phase factor (+) for all the polyads.

** This perturbation theory scheme neglects the terms of the third order of smallness.

Thus, in this work the parameters of the dipole moment function up to the third order were determined simultaneously for the first time. The derivatives obtained in such a way are in closer agreement with the results of recent more accurate *ab initio* calculations[22,23] of the dipole moment functions (Table 4).

The derivative μ_3 turned out to be especially sensitive to contributions of high orders; in the standard scheme of solution of the inverse problem, this derivative was underestimated by an order of magnitude.

Conclusion

For the double transformed operator of dipole moment, the analytical equations are written that relate the parameters of vibrational transition moments of the fundamental bands to molecular constants and allow correct estimation of the first derivatives of the dipole moment. Based on the earlier developed recursion scheme,[5] the set of linear equations was written for determining the derivatives of the dipole moment function up to the third order and the derivatives were found. As experimental data, we took the parameters of vibrational moments for all transitions with $\Delta V \leq 3$. The scheme proposed for determination of the derivatives can be applied to any type of molecules. It was tested with the ozone molecule, for which the ordinary expansion into a series by orders of smallness is fulfilled,[5] and gave the same results as the ordinary scheme.[5] It should be noted that the accuracy of

determination of the derivatives finally depends on the accuracy of determination of the experimental parameters. As the parameters of the transformed dipole moment are refined, the function changes too. In this paper, we did not give the final values for the six third derivatives, but only presented possible versions. The problem of signs for the third derivatives can be solved, when we will have the data on the intensity of difference bands, such as $\nu_1 + \nu_3 - \nu_2$, or reliable values for the rotational corrections to the transition moments. For the H_2S molecule, the intensity distribution in

branches over rotational quantum number has some peculiarities and this problem is still to be solved.

Acknowledgments

APPENDIX

I. Explicit form of functions g for transitions with $\Delta V = 1$

$$g_0^3 = {}^x\mu_e \,/\, \sqrt{2}\left\{\frac{\zeta_{13}^y k_{133} B_y(\omega_1 - \omega_3)}{(\omega_1\omega_3)^{1/2}(2\omega_3 + \omega_1)\omega_1} + \frac{\zeta_{23}^y k_{233} B_y(\omega_2 - \omega_3)}{(\omega_2\omega_3)^{1/2}(2\omega_3 + \omega_2)\omega_2} - 3\,/\,2\sum_{\mu\nu}\frac{k_{\mu\nu\nu}}{\omega_\mu}(S_{3\mu} + S_{3-\mu}) - G_3^y\right\},$$

$$g_1^i = 1\,/\,\sqrt{2}\left\{\begin{array}{l}{}^\alpha\mu_i\left\{1 - \sum_\nu\frac{9k_{i\nu\nu}^2\omega_i\omega_\nu}{(4\omega_\nu^2 - \omega_i^2)^2} - \sum_{i\neq\nu}\frac{9k_{ii\nu}^2\omega_i(\omega_i + \omega_\nu)}{(2\omega_i + \omega_\nu)^2} - \sum_{\mu\nu}\frac{9k_{ii\mu}k_{\mu\nu\nu}}{4\omega_i\omega_\mu}[(i\mu i) + (i-\mu i)] - 2_1 G_{ii}\right\} - \\[2mm] -\sum_{p\neq i}{}^\alpha\mu_p\left[\sum_\nu\frac{9k_{i\nu\nu}k_{p\nu\nu}\omega_\nu\omega_p}{(4\omega_\nu^2 - \omega_i^2)(4\omega_\nu^2 - \omega_p^2)} - \frac{9k_{iip}k_{ipp}(\omega_i + \omega_p)}{\omega_i(2\omega_p + \omega_i)(2\omega_i + \omega_p)}\right] - \sum_{\mu\nu}\frac{9k_{\mu\nu\nu}k_{ip\mu}}{\omega_p\omega_\mu}[(i\mu p) + (i-\mu p)] + \\[2mm] + \left({}_1 G_{ip} + {}_2 G_{pi} - {}_2 G_{ip}\right) - (1 - 2\delta_{i3})\left(S_{ip} + S_{i-p}\right)\end{array}\right\},$$

$$g_2^i = 1\,/\,\sqrt{2}\left\{-\sum_p{}^\alpha\mu_{pp}\left(\frac{6k_{ipp}\omega_p}{4\omega_p^2 - \omega_i^2} + \frac{\delta_{ip}}{\omega_i}\sum_\nu 3k_{i\nu\nu}\right) - \sum_{p\neq i}{}^\alpha\mu_{ip}\left[\frac{3k_{ipp}(\omega_i + \omega_p)}{\omega_p(2\omega_i + \omega_p)} + \frac{1}{2\omega_p}\sum_\nu k_{p\nu\nu}\right]\right\};$$

$$g_3^i = 1\,/\,\sqrt{2}\left\{\frac{1}{2}\sum_p{}^\alpha\mu_{ipp}(1 + 2\delta_{ip)}\right\}.$$

II. Explicit form of functions g for transitions with $\Delta V = 2$

$$g_0^{i3} = -{}^x\mu_e\,/\,2\left\{\frac{\zeta_{i3}^y 2B_y(\omega_i - \omega_3)}{(\omega_i\omega_3)^{1/2}(\omega_3 + \omega_i)}\right\},$$

$$g_1^{ii} = 1\,/\,2\left\{\sum_p\frac{3k_{ipp}}{\omega_p}(i\,i\,p){}^\alpha\mu_p\right\}, \ i\neq j, \ g_1^{ij} = 1\,/\,2\left\{\sum_p\frac{6k_{ijp}}{\omega_p}(i\,j\,p){}^\alpha\mu_p\right\}, \ g_2^{ij} = {}^\alpha\mu_{ij}, \ g_3^{ij} = 0.$$

III Explicit form of functions g for transitions with $\Delta V = 3$

$$g_0^{iii} = {}^x\mu_e\,/\,2\sqrt{2}\left\{\frac{3}{2}\sum_\nu\frac{k_{ii\nu}B_y\zeta_{i\nu}^y}{(\omega_i\omega_\nu)^{1/2}}\left[\frac{(\omega_i + \omega_\nu)}{(\omega_i - \omega_\nu)} - \frac{(\omega_i - \omega_\nu)}{(\omega_i + \omega_\nu)}\right]\right\},$$

$$g_0^{iij} = {}^x\mu_e\,/\,2\sqrt{2}\left\{3\sum_\nu\frac{k_{ij\nu}B_y\zeta_{i\nu}^y}{(\omega_i\omega_\nu)^{1/2}}\left[\frac{(\omega_i + \omega_\nu)}{(\omega_i - \omega_\nu)} - \frac{(\omega_i - \omega_\nu)}{(\omega_i + \omega_\nu)}\right] + \frac{3}{2}\sum_\nu\frac{k_{ii\nu}B_y\zeta_{j\nu}^y}{(\omega_j\omega_\nu)^{1/2}}\left[\frac{(\omega_j + \omega_\nu)}{(\omega_j - \omega_\nu)} - \frac{(\omega_j - \omega_\nu)}{(\omega_j + \omega_\nu)}\right]\right\},$$

$$g_0^{ijl} = {}^x\mu_e / 2\sqrt{2} \left\{ \begin{array}{l} 3\sum_\nu \dfrac{k_{ij\nu}B_y\zeta_{l\nu}^y}{(\omega_l\omega_\nu)^{1/2}}\left[\dfrac{(\omega_l+\omega_\nu)}{(\omega_l-\omega_\nu)(\omega_i+\omega_j+\omega_\nu)}-\dfrac{(\omega_l-\omega_\nu)}{(\omega_l+\omega_\nu)(\omega_i+\omega_j-\omega_\nu)}\right]+ \\[2mm] +3\sum_\nu \dfrac{k_{il\nu}B_y\zeta_{j\nu}^y}{(\omega_j\omega_l)^{1/2}}\left[\dfrac{(\omega_j+\omega_\nu)}{(\omega_j-\omega_\nu)(\omega_i+\omega_l+\omega_\nu)}-\dfrac{(\omega_j-\omega_\nu)}{(\omega_j+\omega_\nu)(\omega_i+\omega_l-\omega_\nu)}\right]+ \\[2mm] +3\sum_\nu \dfrac{k_{jl\nu}B_y\zeta_{i\nu}^y}{(\omega_i\omega_l)^{1/2}}\left[\dfrac{(\omega_i+\omega_\nu)}{(\omega_i-\omega_\nu)(\omega_j+\omega_l+\omega_\nu)}-\dfrac{(\omega_i-\omega_\nu)}{(\omega_i+\omega_\nu)(\omega_j+\omega_l-\omega_\nu)}\right] \end{array} \right\},$$

$$g_1^{iii} = 1/2\sqrt{2}\sum_p {}^\alpha\mu_p\left\{\frac{9}{2}\sum_\nu \frac{k_{ii\nu}k_{ip\nu}}{\omega_p}\left[\frac{(i\,\nu\,p)}{(2\omega_i-\omega_\nu)}-\frac{(i-\nu\,p)}{2\omega_i+\omega_\nu}\right]+G_{iiip}\right\},$$

$$g_1^{iij} = 1/2\sqrt{2}\sum_p {}^\alpha\mu_p\left\{\frac{9}{2}\sum_\nu \frac{k_{ii\nu}k_{\nu ip}}{\omega_p}\left[\frac{(\nu\,j\,p)}{(2\omega_i-\omega_\nu)}-\frac{(\nu-j\,p)}{(2\omega_i+\omega_\nu)}\right]+\right.$$

$$\left.+9\sum_\nu \frac{k_{ij\nu}k_{\nu ip}}{\omega_p}\left[\frac{(\nu\,i\,p)}{(\omega_i+\omega_j-\omega_\nu)}-\frac{(\nu-i\,p)}{(\omega_i+\omega_j+\omega_\nu)}\right]+G_{iijp}\right\},$$

$$i\neq j\neq l,$$

$$g_1^{ijl} = \frac{{}^\alpha\mu_l}{2\sqrt{2}}\left\{ \begin{array}{l} 9\sum_\nu \dfrac{k_{ij\nu}k_{\nu ll}}{\omega_l}\left[\dfrac{(\nu\,ll)}{(\omega_i+\omega_j-\omega_\nu)}-\dfrac{(\nu-ll)}{(\omega_i+\omega_j+\omega_\nu)}\right]+9\sum_\nu \dfrac{k_{il\nu}k_{\nu jl}}{\omega_l}\left[\dfrac{(\nu\,jl)}{(\omega_i+\omega_l-\omega_\nu)}-\dfrac{(\nu-jl)}{(\omega_i+\omega_l+\omega_\nu)}\right]+ \\[2mm] +9\sum_\nu \dfrac{k_{jl\nu}k_{\nu il}}{\omega_l}\left[\dfrac{(\nu\,il)}{(\omega_j+\omega_l-\omega_\nu)}-\dfrac{(\nu-il)}{(\omega_j+\omega_l+\omega_\nu)}\right]+G_{ijll} \end{array} \right\},$$

$$g_2^{iii} = 1/2\sqrt{2}\left\{\frac{2k_{iii}}{\omega_i}{}^\alpha\mu_{ii}+\sum_{p\neq i}\frac{3k_{iip}\omega_p}{(4\omega_i^2-\omega_p^2)}{}^\alpha\mu_{ip}\right\},$$

$$g_2^{iij} = 1/2\sqrt{2}\left\{\frac{12k_{iij}\omega_i}{\omega_j(\omega_j+2\omega_i)}{}^\alpha\mu_{ii}+\frac{6k_{iij}\omega_i}{(4\omega_i^2-\omega_j^2)}{}^\alpha\mu_{jj}+\sum_{p\neq j}\frac{3k_{iip}\omega_p}{(4\omega_i^2-\omega_p^2)}{}^\alpha\mu_{jp}\right\},$$

$$i\neq j\neq l,\ \ g_2^{ijl} = 1/2\sqrt{2}\left\{\left[\frac{6k_{jll}\omega_l}{\omega_j(\omega_j+2\omega_l)}+\frac{6k_{iij}\omega_i}{\omega_j(\omega_j+2\omega_i)}\right]{}^\alpha\mu_{il}+\left[\frac{6k_{ijj}\omega_j}{\omega_i(\omega_i+2\omega_j)}+\frac{6k_{ill}\omega_i}{\omega_i(\omega_i+2\omega_i)}\right]{}^\alpha\mu_{jl}\right\},$$

$$g_3^{iii} = 1/2\sqrt{2}\,,\ \ g_3^{iij} = 1/2\sqrt{2}\,,\ \ g_3^{ijl} = 1/2\sqrt{2}\,,$$

$$(i\pm j\,l) = \frac{\omega_l^2}{(\omega_i\pm\omega_j)^2-\omega_l^2}\,,\ \ S_{i\pm p} = \frac{B_y\zeta_{ip}^y(\omega_i\mp\omega_p)}{2(\omega_i\omega_p)^{1/2}(\omega_i\pm\omega_p)}\,.$$

Equations for G_{ijll} are given in Appendix 2 of Ref. 5:

$$G_3^y = \frac{1}{2\omega_3}\left\{\sum_\nu \mu_{yy}^\nu\zeta_{3\nu}^y\left(\frac{\omega_3}{\omega_\nu}\right)^{1/2}+\frac{3}{2}\sum_{\lambda,\nu}2B_y\left[\frac{k_{\lambda\lambda\nu}\zeta_{3\nu}^y(\omega_3^2-3\omega_\nu^2)}{\omega_\nu(\omega_\nu^2-\omega_3^2)}\left(\frac{\omega_3}{\omega_\nu}\right)^{1/2}+\frac{k_{3\lambda\nu}\zeta_{\nu\lambda}^y(\omega_\lambda-\omega_\nu)}{(\omega_3+\omega_\lambda)^2-\omega_\nu^2}\left(\frac{\omega_\nu}{\omega_\lambda}\right)^{1/2}\right]\right\},$$

$${}_1G_{ij} = \frac{1}{\sqrt{2}(\omega_i+\omega_j)}\times$$

$$\times\left\{\sum_\nu\left[\frac{3k_{ij\nu\nu}}{2}+\frac{B_y\zeta_{i\nu}^y\zeta_{j\nu}^y(\omega_\nu^2-\omega_i\omega_j)}{4\omega_\nu(\omega_i\omega_j)^{1/2}}\right]-\frac{9}{8}\sum_{\lambda,\nu}k_{ij\nu}k_{\lambda\lambda\nu}\left[\left(\frac{1}{\omega_\nu}+\frac{(\omega_i+\omega_j)}{(\omega_i+\omega_j)^2-\omega_\nu^2}\right)+2\frac{k_{i\lambda\nu}k_{j\lambda\nu}(\omega_\lambda+\omega_\nu)}{(\omega_\lambda+\omega_\nu)^2-\omega_i^2}\right]\right\},$$

$$_2G_{ij} = \frac{1}{\sqrt{2}(\omega_i - \omega_j)} \times$$

$$\times \sum_{\nu} \left\{ \left[\frac{3k_{ij\nu\nu}}{2} + \frac{B_y \zeta_{i\nu}^y \zeta_{j\nu}^y (\omega_\nu^2 + \omega_i \omega_j)}{4\omega_\nu (\omega_i \omega_j)^{1/2}} \right] - \frac{9}{8} \sum_{\lambda,\nu} k_{ij\nu} k_{\lambda\lambda\nu} \left[\left(\frac{1}{\omega_\nu} + \frac{1}{\omega_i + \omega_\nu - \omega_j} \right) + 2 \frac{k_{i\lambda\nu} k_{j\lambda\nu} (\omega_\lambda + \omega_\nu)}{(\omega_\lambda + \omega_\nu)^2 - \omega_i^2} \right] \right\}.$$

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