

CALCULATION OF THE DIPOLE MOMENT FUNCTION DERIVATIVES FOR HYDROGEN SULFIDE MOLECULE¹

Hydrogen sulfide (H_2S) spectra present a great interest both for understanding unusual intermolecular processes in this molecule and for remote sounding applications. Since the literature values of H_2S derivatives of the dipole moment function cannot be used for satisfactory calculations of integrated intensities the problem of its finding arises. In this article the back spectroscopic problem for H_2S vibrational spectra has been solved. The pure vibrational part of the effective dipole moment operators is considered. The discrepancies between the transition moment parameters derived from the expression of the integrated intensity and obtained by the traditional scheme for fundamental bands (ν_1 , ν_2 , ν_3) have been revealed. Finally, taking into account the Darling-Dennison and Fermi-type resonance interactions between the vibrational states, the available experimental integrated intensities, and the third-order of the force constants the parameters of the dipole moment function were computed. A good agreement between the obtained values and the latest *ab initio* calculation was found.

Keywords: hydrogen sulfide, dipole moment function, integrated intensities.

Introduction

Detailed information of hydrogen sulfide absorption spectra (H_2S) is important both for investigating of gaseous structure of space objects such as Venus [1] and for understanding physical-chemical processes occurring inside volcanoes [2]. Moreover the remote sounding of H_2S concentration in the Earth's atmosphere based on the H_2S spectra at the atmospheric transparency windows is the actual ecological problem [3]. On the other hand the fundamental significance of the H_2S spectra examining is caused by the specificity for asymmetric top molecules features in its structure.

Since the asymmetric coefficient of H_2S equals $\kappa = 0,5234$ then this molecule has the properties which cannot be related neither to prolate tops ($\kappa = -1$) nor to oblate tops ($\kappa = 1$). Therefore similarly to H_2O molecule ($\kappa = -0,4362$) there are strong resonance effects which result in the forming fourfold clusters in the vibrational-rotational (VR) H_2S energy levels [4]. Centrifugal distortion effects lead to the unusual distribution of the intensity values between the branches of the fundamental bands ν_1 and ν_2 : the lines of the *P*-branch are weaker than the *R*-branch [5, 6]. In addition, the intensity of lines corresponding to the transitions with $\Delta K = 2$ which according to the perturbation theory are assumed as less probable can be exceed the transitions with $\Delta K = 1$ in ν_3 band [7].

From the analysis of experimental spectra it is also concluded that the intensity of lines of the combination bands: $\nu_1+\nu_2$ and $\nu_2+\nu_3$ have the larger values in a comparison with the intensity of the fundamental bands: ν_1 and ν_3 [8]. That is valid for its integrated values too. Hence the second-order derivatives of the dipole moment function are comparable with the first ones. According to the traditional scheme of calculating the VR-spectra of asymmetric tops the value of the integrated intensity depends only on the square of the transition moment parameter that is the parameter of the effective dipole moment in the power expansion by vibrational and rotational operators. In this work the discrepancy in the value of the transition moment parameter obtained with the centrifugal distortion operators and calculated by the solution of the pure vibrational problem is showed. It is clear that the parameters (derivatives) of the dipole moment function are different for various values of the transition moment parameters. Finally, the fact that the parameters of the dipole moment function determined on the basis of the experimental values of the integrated intensities are closed to the last *ab initio* calculation results [9] without of including the third-order derivatives [10] is established.

Method

The calculations in this paper are carried out on the basis of the effective operator formalism. Under this approach the projection $\tilde{\mu}_z$ of the effective (transformed) dipole moment is associated with the same projection in a space-fixed coordinate system by means of unitary transformations which are the ana-

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logues of reducing the effective VR-Hamiltonian. Thus, the obtained expression is the series by vibrational and rotational operators which for a certain vibrational transition ($v \rightarrow v'$) of XY_2 type molecules has the form [11]:

$$\langle v | \tilde{\mu}_z | v' \rangle = \sum_{\alpha} {}^{\alpha}\tilde{\mu}^{vv'} \varphi_{\alpha} + \sum_{\alpha, \beta} {}^{\alpha, \beta}\tilde{\mu}^{vv'} \frac{1}{2} \{ \varphi_{\alpha}, J_{\beta} \} + \sum_{\alpha, \beta, \gamma} {}^{\alpha, \beta, \gamma}\tilde{\mu}^{vv'} \frac{1}{2} \{ \varphi_{\alpha}, J_{\beta} J_{\gamma} \} = \sum_j {}^j\tilde{\mu}^{vv'} A_j^{vv'}, \quad (1)$$

where ${}^j\tilde{\mu}^{vv'}$ – some parameters; $A_j^{vv'}$ – the operators are determined by the type of transitions [8]. The parameter ${}^{\alpha}\tilde{\mu}^{vv'}$ in expression (1) is called a transition moment parameter (TMP) corresponds to the vibrational part of the transformed dipole moment. In the case of arbitrary transitions with $\Sigma \Delta v \leq 2$ the expression for ${}^{\alpha}\tilde{\mu}$ has the following view [11]:

$${}^{\alpha}\tilde{\mu} = {}^{\alpha}\mu_e + \sum_a {}^{\alpha}\mu_a q_a + \sum_{a \leq b} \left({}_{(2)}^{\alpha}\tilde{M}_{ab} q_a q_b + {}_{(2)}^{\alpha}\tilde{M}^{ab} p_a p_b \right), \quad (2)$$

where ${}^{\alpha}\mu_e$ – permanent dipole moment constant; ${}^{\alpha}\mu_a$ – the first-order derivatives of the dipole moment function; ${}_{(2)}^{\alpha}\tilde{M}_{ab}$ and ${}_{(2)}^{\alpha}\tilde{M}^{ab}$ – expressions depending on the first and the second-order derivatives of the dipole moment function and to the third-order of the potential function parameters.

Using the effective wave functions the vibrational and rotational contributions can be separated in the total expression for the intensity of VR-lines. Hence the integrated intensity value can be estimated by the following formula:

$$S_v = \frac{8\pi^3}{3hcZ_v(T)} v_0 \left(1 - \exp \left[-\frac{v_0 hc}{kT} \right] \right) \exp \left[-\frac{E_v hc}{kT} \right] |{}^{\alpha}\tilde{\mu}^{vv'}|^2, \quad (3)$$

where v_0 – the band center; Z_v – the vibrational statistical sum [12]; E_v – the energy of the low vibrational state; T – temperature; h, c, k – the well-known constants.

The vibrational energy levels of the asymmetric top molecules can be found by the diagonalization of the effective vibrational Hamiltonian matrix [13] containing the nondiagonal elements which take into account the Darling-Dennison and Fermi-type resonance interactions. It allows one to consider the effects of resonance interactions in the integrated intensity value.

Results

The values of the experimental integrated intensities presented in Table 1 and the parameters of the potential function of the third-order from work [14] are used for solving the back spectroscopic problem. The vibrational energy levels of the investigated bands are calculated by means of the effective vibrational Hamiltonian with the parameters [13]. According to the results demonstrated in table 1 the TMP

Table 1
Experimental values of H_2S integrated intensities ($T = 296$ K)
and corresponding to them the value TMP (in Debye)

Band	$S_v^{exp},$ $cm^{-1}/(molecul \cdot cm^{-2})$	The value of TMP, ${}^{\alpha}\tilde{\mu}^{vv'} \cdot 10^{-2}$	
		Initial	Formula (3)
v_1	$1,824 \cdot 10^{-20}$ [8]	0,29383₁₂ [8]	0,410
v_2	$8,431 \cdot 10^{-20}$ [6]	-0,969₀ ± 0,050₀ [10]	-1,314
v_3	$4,843 \cdot 10^{-21}$ [8]	0,02193₁₃ [8]	0,211
$2v_1$	$9,276 \cdot 10^{-21}$ [15]	$0,215_5 \pm 0,021$ [10]	0,209
$2v_2$	$1,337 \cdot 10^{-20}$ [8]	$-0,34770_{15}$ [8]	-0,370
$2v_3$	$1,539 \cdot 10^{-21}$ [15]	$0,090_2 \pm 0,026$ [10]	0,084
v_1+v_2	$7,339 \cdot 10^{-20}$ [8]	$0,68306_{14}$ [8]	0,684
v_1+v_3	$1,960 \cdot 10^{-20}$ [15]	$-0,311_6 \pm 0,050$ [10]	-0,303
v_2+v_3	$1,157 \cdot 10^{-19}$ [8]	$0,88751_{16}$ [8]	0,859

of ${}^6\mu^{000-001}$ parameter equals $3,3668 \cdot 10^{-4}$ D that exceeds the transition moment value ($2,193 \cdot 10^{-4}$ D). As can be seen from table 1 the centrifugal distortion effects are also essential for probabilities of VR-transitions into the energy levels of v_1 и v_2 states. At the same time, with respect to the v_2 is difficult to assess their role as there are no accurate experimental data of the intensities in this spectral region.

The parameters of the dipole moment function to the second-order of perturbation theory calculated by the least square method on the basis of the obtained in this study TMP are shown in Table 2 (the results of calculations are based on the initial TMP fully comply with [10] and are not shown here). In column *c* the set of parameters obtained without resonances is presented. For the results in column *d* the resonance interactions were taken into account. From comparing of two results it is seen that for the investigated experimental bands the resonance influence is not essential. As expected, the new values of the TMP particularly change the ${}^z\mu_3$ parameter and make the result equivalent to work [10] where the third-order derivatives were taken into account. It should be noted that the signs of TMP for all polyads were supposed positive as in [10].

Table 2
The H₂S dipole moment function parameters, $D \cdot 10^{-3}$

Parameter	Perturbational calculations				<i>Ab initio</i> calculation
	[10]		This work		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	Set I [9]
${}^x\mu_1$	1,60	4,16 [11]	5,80	5,82	2,998
${}^x\mu_2$	−21,1	−13,7 [11]	−18,6	−18,6	−21,574
${}^z\mu_3$	3,00	0,3 [11]	2,98	2,98	1,881
${}^x\mu_{11}$	3,20	3,2	3,32	3,448	2,929
${}^x\mu_{12}$	13,9	13,9	13,86	13,79	13,894
${}^x\mu_{22}$	−4,8	−4,8	−4,70	−4,68	−4,546
${}^z\mu_{13}$	−5,8	−5,8	−5,42	−5,42	−4,174
${}^z\mu_{23}$	15,7	15,7	16,52	16,52	16,259
${}^x\mu_{33}$	1.4	1.4	2.46	2.08	0.012

a – the third-order derivatives were included in the expression (2); *b* – derivatives of the second-order were included; *c* – results were obtained without of accounting the resonance interactions; *d* – resonance interactions were taken into account.

Conclusions

In this paper the new set of the dipole moment function parameters suitable for the calculation of H₂S integrated intensities was developed. The significant impact of centrifugal distortion effects on the VR-transition probabilities in ν_3 band was found.

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