The local mode effect and the ambiguity of the rovibrational wavefunctions calculation for the hydrogen sulfide molecule

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The local mode effect observed in the experimental spectrum of hydrogen sulfide molecule in the 8400–8900 cm^{-1} region has been studied. This effect causes formation of the fourfold energy clusters of Type II. In the course of the spectrum analysis it has been shown that the wavefunctions corresponding to fourfold clusters are defined ambiguously from the energy level fitting, which results in ambiguity in calculation of the transition intensities. It is shown that the ambiguity can be eliminated using the experimental information about transition intensities.

Introduction

Investigation of absorption spectra of the H_2S molecule and its isotopologues are of particular interest for atmospheric spectroscopy, because the infrared radiation absorption by hydrogen sulfide affects radiation properties of atmosphere. It is well known that sulfur-containing compounds, H_2S among them, are typical products of volcanic activity. Spectroscopic data on the molecule are included into the HITRAN database, as well as into SPECTRA and ATMOS information systems.

When solving the inverse problem on determination of rotational, centrifugal, and resonance constants for highly-excited vibrational states of the hydrogen sulfide, there appear some difficulties connected with the energy level degeneracy resulting in an ambiguity in determination of wavefunctions, which, in turn, leads to an ambiguity in calculations of line intensities.

The equilibrium configuration of the hydrogen sulfide in the ground electronic state, its force field, and the proportion between atom masses are such that the rovibrational (RV) energy spectrum turns to be close to the local mode limit for molecules of $XY_2(C_{2v})$ type. In this case, the vibrational excitation is localized on one of the bonds XY with very large time of energy migration to another bond. In such a way, the vibrational spectrum is a consequence of closely located levels (local mode pairs). The growing vibrational excitation leads to almost total degeneration.[1] When accounting for the molecule rotation in the rovibrational energy spectrum, a fourfold degeneration of two types is observed.[2] The first type of clusterization is stipulated by centrifugal forces and is observed at high values of the quantum number of the angular momentum J. This phenomenon was first studied in Ref. 3. Transitions to such states are weak, and the experimental investigation of this clusterization type is difficult. The second type of the fourfold clusterization results from degeneration in the local mode pairs, which are formed by vibrational states of the symmetry of different types at a high excitation of valence vibrations. This clusterization type is easily observed in the near-infrared range both at small and large J values.

The fourfold clusterization strongly affects the formation of rotational structure of spectrum for polyades of interacting vibrational states close to the local mode limit. In particular, the spectrum of the H_2S molecule with the point symmetry group C_{2v} becomes similar to the spectrum of a molecule of a lower symmetry group C_s. In many recent publications (Refs. 4–13, for example) the rotational structure of H_2S vibrational states within the local mode limit has been studied. However, much less is known about intensities of transitions to the states involved into the fourfold clusters. When solving the inverse problem, a strong resonance interaction between the levels with close energies, included into the clusters, results in unstable determination of resonance parameters through the fitting and, consequently, in some arbitrariness in mixing coefficients of wavefunctions. As a result, there appears an ambiguity in calculations of spectral line intensities, which can cause a significant disagreement between calculated and experimental intensity values.

In this work, the fourfold clusterization of Type II is studied and the line intensity distribution in such clusters is analyzed relying on the H_2S molecule spectrum around 1.1 μm.

1. Local mode effect in highly excited states of the hydrogen sulfide molecule

The H_2S absorption spectra formed by transitions to RV levels of the local mode pairs were recorded with the intracavity,[7–11] diode,[5] and Fourier spectrometers.[4,6,12,13] The manifestation of the local mode effect for highly excited vibration states (301)–(202) and (311)–(212) was first found, when the H_2S Fourier spectrum was studied in a wide spectral range

between 2 000 and 11 147 cm^{-1} (Ref. 4). The rotational structure of the energy spectrum of these local pairs is totally identical beginning with $J = 0$, and the difference between energy levels in the local pairs does not exceed the experimental error. Fourfold clusters of Type II were observed in the energy spectrum already at $J = 4$, $K_a = 0$ and 1. Rotational and centrifugal distortion parameters for components of the local mode pair were determined from fitting under condition of equality between them. The presented mixing coefficients of wavefunctions for fourfold clusters sharply changed between 1 and 50%, which confirms their unstable determination through fitting.

The H$_2$S local mode pairs $(60^{\pm}, 0)$, $(50^{\pm}, 1)$, $(70^{\pm}, 0)$, $(50^{\pm}, 0)$ with identical rotational structures were studied near 14100—14400 (Ref. 7), 13060—13357 (Ref. 8), 16180—16440 (Ref. 10), and 11930—12300 cm^{-1} (Ref. 5), respectively. In this case the absence of the Coriolis resonance due to the H$_{21}$ = C$_y$(iJ_y) member in operator of interaction between the local mode pair components, i.e., so called "quenching," predicted theoretically,[14] has been evidenced.

In Ref. 6, based on the experimental data from Refs. 4 and 5, it was first shown that for the $(40^{\pm}, 1)$, $(50^{\pm}, 0)$ states of H$_2$S the local mode limit is realized,[14] when the resonance interaction between components of the local mode pair disappears totally. In this case, instead of two sets of energy levels corresponding to the local mode pair components, one set may be constructed taking into account the ambiguity in rovibrational assignment, which then can be attributed to a hypothetical isolated vibration state of molecule of the C$_s$ symmetry.

Large sets of the energy levels were retrieved for the $(40^{\pm}, 0)$ and $(40^{\pm}, 1)$ local mode pairs from the spectrum analysis in the 9540—10000 and 10780—11330 cm^{-1} regions in Refs. 9 and 11, where it was stated for the first time that the local mode rotational structure is not always stable as the rotational quantum numbers J and K_a grow. Resonance interactions of components of a local mode pair with other states close in energies can destroy the cluster structure of the energy spectrum, which was shown, for example, in Ref. 9 and will be further demonstrated in our paper. The wavefunctions, obtained while calculating energy levels for the $(40^{\pm}, 1)$ local mode pair both with accounting for strong interaction between its components and in the case of complete resonance quenching,[9] were used to model intensities of the observed transitions. This has led to the conclusion that only those wavefunctions, which were determined with accounting for resonance interactions, allow an adequate calculation of intensities.

Fourfold clusters of Type II were first predicted by Lexmann, who studied local modes in molecules of the H$_2$X type.[15] A detailed and successive introduction in the local mode theory is given in Ref. 1. The RV Hamiltonian in natural coordinates is written in Ref. 14, where it is also shown that the off-diagonal term, responsible for resonance interaction between local mode pair components, can be transformed into diagonal one, providing the equality

between α_1 and α_3 rovibrational constants determining the vibrational dependence of rotational constants:

$$A = A_0 + \sum_i \alpha_i \left(v_i + \frac{1}{2} \right). \qquad (1)$$

The manifestation of the local mode effect in H$_2$S and similar molecules with a heavy central atom (H$_2$Se and H$_2$Te) is discussed in Ref. 2 in terms of the "global" variational calculation. It is shown that in case of a negligibly small difference between cluster components (full degeneration of cluster states) the cluster can be presented by four dimensional space of the degenerated wave eigenfunctions of the rovibrational Hamiltonian. A certain choice of basic vectors in this space gives a simple pattern of the molecular movement in the local mode limit: the valence vibrational excitation is localized on one of the bonds and the molecule rotates around this bond, while the second bond is almost perpendicular to the rotation axis and lengthens as J grows due to centrifugal distortion, in fact, leading to the molecule symmetry lowering from C$_{2v}$ to C$_s$.

2. Peculiarities in modeling H$_2$S absorption line intensities in the region of the second decade of interacting states

The hydrogen sulfide infrared Fourier spectrum within 8400—8900 cm^{-1} is to a significant extent formed by transitions to upper vibrational states (211) and (112) belonging to the second decade. The inverse problem was solved simultaneously for 7 vibrational states presented in Table 1.

Table 1. Experimental and calculated energy levels (cm^{-1}) of H$_2$S molecule in the region of the second decade

Normal modes	Local modes	E_{cal}, cm^{-1}	E_{exp}, cm^{-1}
v_1 v_2 v_3	$mn \pm$, v		
1 3 1	20–, 3	8539.428	8539.561
2 3 0	20+, 3	8539.672	8539.925
0 3 2	11+, 3	8637.174	8637.174
1 1 2	30+, 1	8697.143	8697.142
2 1 1	30–, 1	8697.129	8697.155
3 1 0	21+, 1	8878.316	—
0 1 3	21–, 1	8897.426	—

Note that transitions to dark states (013) and (310) were not recorded experimentally, but were included into processing as being involved into resonance interactions with (112) and (211). States of the polyade under consideration are connected by the Coriolis, Fermi, and Darling—Dennison resonances. In addition to these accidental resonances, typical for molecules of XY$_2$(C$_{2v}$) type, there can appear other resonance interactions caused by strong vibrational excitation. To identify and model the spectrum, the method of effective Hamiltonians and effective dipole moments was used.[13]

It is seen in Table 1 that among the considered states there is a local mode pair (211)–(112) with almost coinciding vibrational energies 8697.155 and 8697.142 cm^{-1}. As a result of spectrum identification within the considered region, a vast set of experimental energy levels for the (211) and (112) states was determined. Table 2 presents rovibrational energy levels for $J = 4$, where four- and double-level clusters can be seen.

Table 2. Rotational energy levels belonging to the (211) and (112) vibrational states of H$_2$S

$J K_a K_c$	Energy, cm^{-1}	
	(211)	(112)
4 0 4	8806.6371	8806.6182
4 1 4	8806.6478	8806.6218
4 1 3	8841.4072	8841.4162
4 2 3	8841.0678	8841.0771
4 2 2	8863.2876	8863.2717
4 3 2	8867.5318	8867.5230
4 3 1	8875.8505	8875.8364
4 4 1	8890.4453	8890.4553
4 4 0	8891.4384	8891.4442

As is seen in Fig. 1, for $J = 4$ the rotational energy structure of the local mode pair components is still identical, but as J grows, the doublet cluster structure destroys because of interaction of the components with other vibrational states.
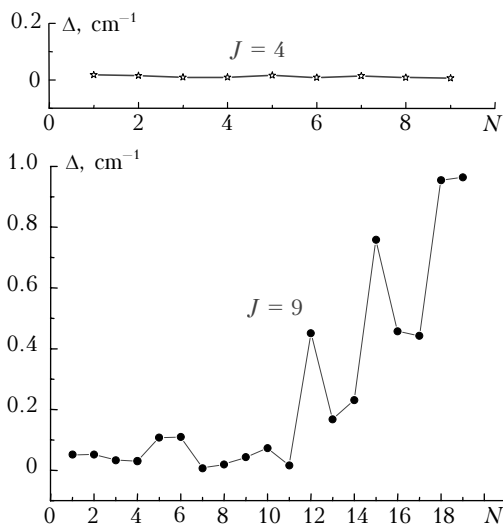

Fig. 1. Degradation of the cluster structure of energy levels of the local mode pair (211), (112); $N = J + K_a - K_c + 1$; $\Delta = |E_{211} - E_{112}|$.

In our case, the (211) vibrational state interacts with the (032), which is not included into the local mode pair, through the Coriolis resonance, and the (112) is connected with the (032) through a weak Fermi resonance. Because of this nonsymmetrical interaction the energy levels of the local mode pair are shifted differently. This results in elimination of the doublet degeneracy.

Spectroscopic constants for the H$_2$S second decade were determined by the least squares method from

fitting to experimental values at a mean calculation accuracy about 0.006 cm^{-1} for energy levels and 15% for line intensities. Mixing coefficients of wavefunctions were calculated as

$$S_{JK_aK_cvv'} = \sum_k \left|C_k^{vv'}\right|^2, \qquad (2)$$

where $C_k^{vv'}$ are expansion coefficients over symmetric top wavefunctions.

These coefficients determine "a share" of the vibrational state v' in the wavefunction of the RV-level vJK_aK_c.

When solving the inverse problem, it was noticed that the mixing coefficients of wave functions for energy levels of the local mode pair $(30^\pm, 1)$, forming the fourfold clusters, differ significantly (by tens of percent) values for different (but very close in values) sets of rotational, centrifugal, and resonance Hamiltonian parameters, which is seen from Table 3 and Fig. 2.

Table 3. Energy levels and wave function mixing coefficients of H$_2$S for two sets of Hamiltonian parameters

$J K_a K_c$	E_{211}, cm^{-1}	Calculation 1		Calculation 2		E_{112}, cm^{-1}
		MC$_1$, %		MC$_2$, %		
		(211)	(112)	(211)	(112)	
6 0 6	8915.0364	87.9	12.0	51.9	48.0	8915.0700
6 1 6	8915.0364	87.7	12.2	52.3	47.5	8915.0700
6 1 5	8969.5649	95.8	4.0	74.1	25.8	8969.5634
6 2 5	8969.5310	73.3	26.6	61.8	38.1	8969.5426
6 2 4	9013.6931	82.1	17.8	88.1	11.8	9013.6864
6 3 4	9013.4180	76.5	23.4	84.1	15.8	9013.4093
6 3 3	9048.3798	59.6	40.3	66.2	33.7	9048.4064
6 4 3	9045.0261	52.0	47.9	58.1	41.8	9045.0030
6 4 2	9063.7933	73.2	26.7	69.8	30.1	9063.8205
6 5 2	9077.9598	58.8	36.9	54.2	41.8	9077.8754
6 5 1	9081.4517	76.1	20.7	73.8	23.3	9081.5230
6 6 1	9109.1533	85.6	14.3	83.7	16.2	9109.1149
6 6 0	9109.3553	87.6	12.2	86.1	13.8	9109.3176

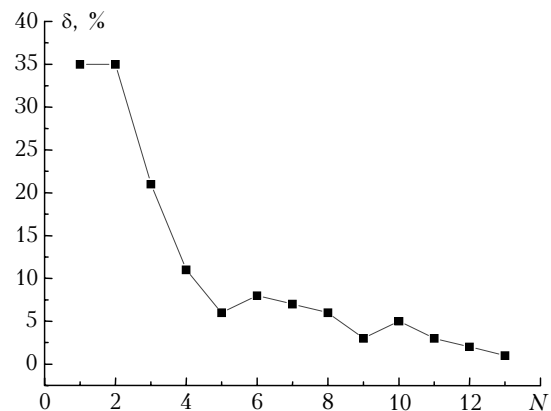N o t e . MC is the mixing coefficient of wave functions.

Fig. 2. Ambiguity in determination of wavefunction mixing coefficients for two sets of H$_2$S Hamiltonian parameters, $N = J + K_a - K_c + 1$; $\delta = |MC_1 - MC_2|$.

As a consequence, values of calculated intensities for transitions to cluster levels change dramatically for different realizations of wavefunctions, although their sum remains unchangeable.

It must be said that local mode pairs are formed also for lower-located polyades, for example, for the first decade[16,17] the local mode pair (201)–(102) with vibrational energies 7576.547 and 7576.383 cm^{-1}, as well as the (121)–(220) with 7420.093 and 7419.616 cm^{-1} energies are formed, linked by strong resonance interactions of the Coriolis type. In this case the rotational structure of local mode pairs is not exactly identical yet; and when solving the inverse problem, the ambiguity does not arise in determination of wave functions.

At last, at total degeneracy of energy levels included into the cluster (as it is for the local mode pairs from Section 1), transitions to cluster levels also turn to be fourfold degenerated and form one experimental line. In this case, a summarized intensity of the line formed by four degenerated transitions is recorded in the experiment. The total calculated intensity is independent of distribution of calculated intensities between cluster components and, consequently, is insensitive to large variations in the mixing coefficients.

In the intermediate case, considered in this paper, the fourfold clusters (see Table 3) are composed of two degenerated doublet levels, the difference between which reaches 0.04 cm^{-1}. As a consequence, transitions to the fourfold clusters correspond to two doublet lines which are apart by the same 0.04 cm^{-1}. Such doublets were observed in the studied Fourier spectrum as two very close lines with different intensities. In the given case the experimental intensities determine what distribution of calculated intensities between local pair components must take place.

Let us consider two doublet lines observed in the spectrum as an example. One doublet centered at 8748.69 cm^{-1} is formed by transitions [606]–[515] and [616]–[505] to the state (112); another doublet centered at 8748.73 cm^{-1} corresponds to transitions [616]–[515] and [606]–[505] to the state (211). Figure 3 shows that wave functions, corresponding to calculation 1, adequately reproduce the experimental intensities, while the calculation 2 gives wavefunctions, the mixing coefficients of which do not allow the adequate calculation of line intensities. The summarized intensity of doublet lines in calculations 1 and 2 remains the same.

To overcome difficulties in line intensity calculations, when solving the inverse problem, a simultaneous fitting of energy levels and intensities to experimental values is required, i.e., a simultaneous minimization of the functionals ε and σ, describing the quality of calculation of intensities and energy levels, respectively:

$$\varepsilon = \left\{ \sum_{i=1}^{N} \frac{\left[\left(I_i^{\mathrm{calc}} - I_i^{\mathrm{obs}} \right) / I_i^{\mathrm{obs}} \right]^2}{N - L} \right\}^{\frac{1}{2}}, \qquad (3)$$

where I_i^{obs} and I_i^{calc} are the experimental and calculated transition intensities; N is the total number of experimental data; L is the number of the used parameters;

$$\sigma = \left\{ \sum_{i=1}^{N} \frac{\left(E_i^{\mathrm{calc}} - E_i^{\mathrm{obs}} \right)^2}{N - L} \right\}^{\frac{1}{2}}, \qquad (4)$$

E_i^{obs} and E_i^{calc} are the experimental and calculated energy levels. However, such experimental fitting is a very cumbersome procedure; and we do not know any examples of its realization in the scientific literature.
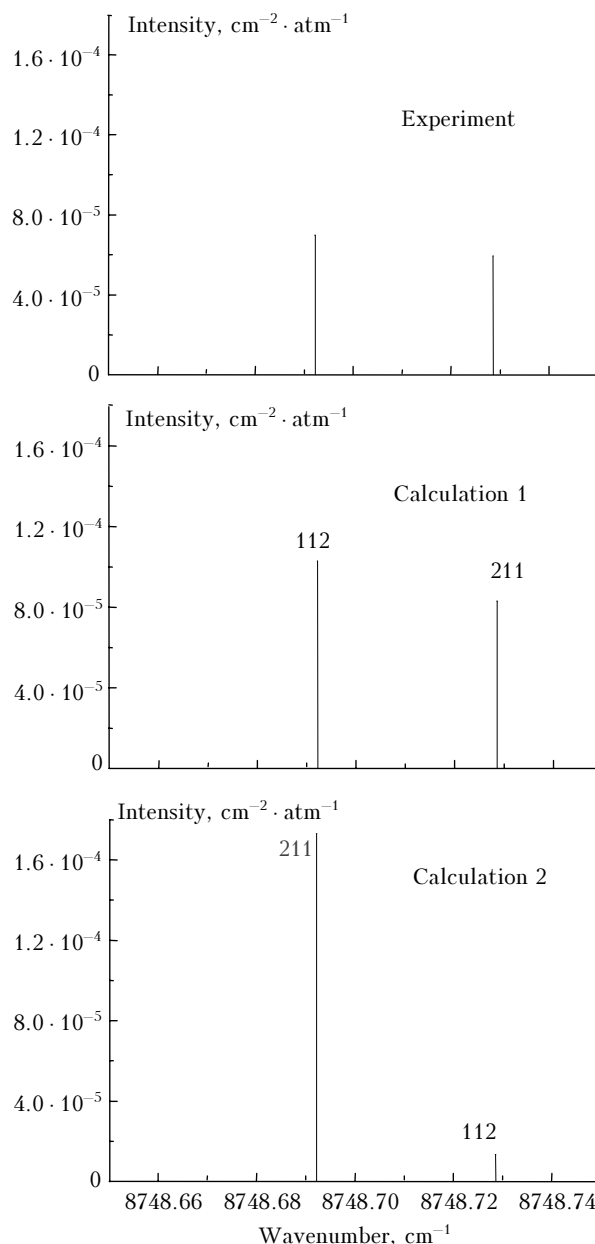

Fig. 3. Experimental and calculated H$_2$S intensities for two different sets of Hamiltonian parameters.

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In our case, when the energy levels included into the fourfold cluster are not totally degenerated and the corresponding lines are observed in the spectrum, the experimental intensities for each doublet line can be used as a criterion of adequacy of the transition intensity calculations. This means that the fitting of rotational, centrifugal, and resonance constants can be performed under condition that the derived wavefunctions are simultaneously tested for adequacy of calculation of experimental intensities.

In parallel with our work,[13] the second decade of the H_2S interacting states was investigated in Ref. 12, where one more peculiarity in behavior of the intensity of transitions was first marked: a disappearance of spectrum lines corresponding to $[J-1\ 1\ J-1]-[J\ 0\ J]$, $[J-1\ 0\ J-1]-[J\ 1\ J]$ transitions of the P-branch of (112)–(000) band for $J \geq 4$. Evidently, this effect is due to the strong resonance interaction between local mode pair components.

Conclusion

Based on literature data and original results, it is shown in this work that a pronounced effect of local modes is observed in the experimental spectrum of the hydrogen sulfide molecule higher than 8400 cm^{-1}. This means that the rotational energy structure of the local mode pairs becomes identical, forming two- and fourfold energy level clusters; and the H_2S spectrum becomes formally similar to the spectrum of hybrid bands of a molecule of the C_s symmetry, when the transitions of A and B types are simultaneously observed. However, as is seen from the reviewed experimental information on energy levels, the cluster local mode structure is not stable: it sooner or later is destroyed because of resonance interactions with other close in energy states.

From the point of view of studying the molecule dynamics in the local mode limit, the case of a quasilocal mode pair is of a particular interest. In this case the energy levels of the pair's components differ by the magnitude exceeding the spectrometer resolution. As a result, series of closely located doublet lines appear in the spectrum. Wavefunctions of levels involved into the fourfold clusters are determined ambiguously. As is shown in our work, the ambiguity can be eliminated by a proper choice of rotational and resonance constants, using as the criterion the quality of the experimental intensity reproduction for transitions involving the cluster levels.

However, solving the inverse problem independently for line centers and intensities is a standard practice in the scientific literature up to now. So, for example, in the above-cited work[12] devoted to the H_2S spectrum identification in the second decade region, the fitting of energy levels and determination of rotational, centrifugal, and resonance constants were made without any estimation of the adequacy of the obtained data for the line intensity calculation.

Thus, the inverse problem for energy levels should be solved at least in parallel with intensity modeling for the molecule in the local mode limit. Transitions to fourfold clusters form the strongest lines in the hydrogen sulfide spectrum in the range higher than 8000 cm^{-1}, and the correct calculation of their intensities is important for estimates of the H_2S integral absorption.

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