OPTICS AND SPECTROSCOPY

HIGH-RESOLUTION SPECTRUM OF THE FIRST TRIAD OF D$_2^{32}$S INTERACTING STATES

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The high-resolution spectrum of the D$_2$S molecule registered with a Bruker IFS 120HR Fourier spectrometer in the range 2000–4200 cm$^{-1}$ is analyzed. The spectroscopic parameters of the (110), (011), and (030) vibrational states are obtained. They reproduce rotational energy levels with the accuracy close to experimental one (a total of 737 rovibrational energies is considered corresponding to 2590 transitions up to $J^\text{max} = 21$).

Keywords: rovibrational spectra, spectroscopic parameters, inverse spectroscopic problem.

Rovibrational spectroscopy of hydrogen sulfide including its isotopes, for example D$_2$S, is of interest for several reasons. On the one hand, investigation of spectra of the given molecule is important for monitoring of the Earth and planet atmospheres [1]. On the other hand, the molecule is of interest from the theoretical viewpoint, because it is one of the lightest asymmetric top molecules. As a consequence, many spectroscopic effects and special features inherent in asymmetric tops are most strongly manifested exactly in its spectra. Moreover, hydrogen sulfide serves as an object of investigation also because it belongs to molecules for which the local mode approximation is fulfilled. Thus, the hydrogen sulfide molecule and its doubly deuterated isotopes can be considered as a good test for various methods used in physical chemistry to determine the potential function and dipole moment and to extract information from rovibrational spectra (see [2–9]).

The D$_2$S molecule has been studied in many works (for example, see [10–20]). However, only few of them studied high-resolution spectra in the infrared range. In particular, the rotational structure of the ground vibrational state was investigated in [18]. Three fundamental $v_1$, $v_2$, and $v_3$ bands were registered experimentally and analyzed in [17, 19]. Two lower combination bands $v_1 + v_2$ and $v_2 + v_3$ belonging to the triad $v = 3/2$ ($v = v_1 + v_2/2 + v_3$) were discussed in [20].

In the present article, new information on the interacting $v_1 + v_2$ and $v_2 + v_3$ bands is presented, and for the first time, the 3$v_2$ band of the doubly deuterated hydrogen sulfide molecule is analyzed.

The D$_2$S spectra investigated in this work were registered with a Bruker IFS 120HR Fourier spectrometer in the range 2000–4200 cm$^{-1}$ at room temperature (297±1) K in the National Laboratory of Synchronous Radiation of China University of Sciences and Technologies (Hefei). Measurements were carried out under different conditions to record strong and weak lines of the spectrum. Since the examined sample was a mixture of hydrogen sulfide and its singly and doubly deuterated isotopes, transitions of all three molecules D$_2$S, HDS, and H$_2$S in the 3.0% H$_2^{32}$S: 23.5% HD$^{32}$S: 68.7% D$_2^{32}$S: 0.5% D$_2^{33}$S: 1.0% HD$^{34}$S: 3.0% D$_2^{34}$S ratios were present in the spectra. Calibration was performed according to H$_2$O and CO$_2$ lines (HITRAN2004 data [21]). The accuracy of positioning of nonoverlapped strong lines was estimated to be 0.001 cm$^{-1}$ for lower frequencies of the spectrum (~2000–2500 cm$^{-1}$) and 0.002–0.003 cm$^{-1}$ in the range ~3000–4000 cm$^{-1}$.

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The D$_2$S molecule is a planar three-atomic molecule of symmetry $C_{2v}$. This means that its three vibrational coordinates are transformed according to the following representations: $q_1$ ($\lambda = 1, 2$) $\in A_1$ and $q_3$ $\in B_1$. Therefore, the (110) and (030) states possess symmetry $A_1$, the (011) state has symmetry $B_1$, and the selection rules for rovibrational transitions are the following:

$$\Delta J = 0, \pm 1, \quad \Delta K_a = \pm (2n + 1), \quad \Delta K_c = \pm (2m + 1)$$

(1)

for the $b$-type transitions of $v_1 + v_2$ and $3v_2$ bands and

$$\Delta J = 0, \pm 1, \quad \Delta K_a = \pm 2n, \quad \Delta K_c = \pm (2m + 1)$$

(2)

for the $a$-type transitions of the $v_2 + v_3$ band.

Since the upper states of the $v_1 + v_2$ and $v_2 + v_3$ bands have different symmetry types and positions of their centers differ only by 11.8 cm$^{-1}$, the strong Coriolis resonance is observed. The resonant interaction is so strong that already at $J = 2$, it is impossible to obtain physically reasonable values of the rotational constants reproducing the energy levels in the model of the (110) and (011) isolated vibrational states with sufficient accuracy. Possible influence of other vibrational states is disregarded because they are far enough, except for the nearest $3v_2$ band of the same triad localized $-200$ cm$^{-1}$ below. Therefore, in the present study we took advantage of the Hamiltonian in the form

$$H^{v-v'} = \sum_{vv'} |v}\langle v'|H^{vv'}.$$  

Here $|v\rangle$ and $|v'\rangle$ designate the interacting states of the examined triad, $H^{v}$ is the operator describing the rotational structure of the vibrational states $|1\rangle = (110)$, $|2\rangle = (030)$, and $|3\rangle = (011)$. Diagonal terms of the $H^{v}$ operator $H^{v-v'}$ is represented by the Watson Hamiltonian [22] of the following form (where $A$ denotes reduction and $I_r$ denotes representation):

$$H^{v} = E^{v} + \left[ A^{v} \frac{-1}{2} (B^{v} + C^{v}) \right] J_z^2 + \frac{1}{2} (B^{v} + C^{v}) J^2 + \frac{1}{2} (B^{v} - C^{v}) J_y^2$$

$$-\Delta_J^2 J_z^2 - \Delta_J J_z^2 J^2 - \Delta_J J^4 - 8 \delta_K \left[ J_z^2 (J_z^2 - J_y^2) \right] - 2 \delta_J J^2 (J_z^2 - J_y^2)$$

$$+ H^{v}_{KK} J_y^6 + H^{v}_{JJ} J_y^4 J^2 + H^{v}_{Jr} J_y^2 J^4 + H^{v}_{r} J_y^6 + \left[ (J_z^2 - J_y^2), h^{v}_{K} J_z^4 + h^{v}_{r} J_z^2 J_z^2 + h^{v}_{r} J_y^4 \right]$$

$$+ L^{v}_{K} J_y^8 + L^{v}_{KK} J_y^4 J^2 + L^{v}_{JJ} J_y^2 J^4 + L^{v}_{r} J_y^6$$

$$+ \left[ (J_z^2 - J_y^2), h^{v}_{K} J_z^4 + h^{v}_{r} J_z^2 J_z^2 + h^{v}_{r} J_y^4 \right]$$

$$+ P^{v}_{K} J_y^{10} + P^{v}_{KK} J_y^2 J^2 + P^{v}_{JJ} J_y^4 J^2 + \ldots + \left[ (J_z^2 - J_y^2), p^{v}_{K} J_y^8 + \ldots \right]$$

(4)

Nondiagonal operators $H^{v-v'} (v \neq v')$ describe the resonant Coriolis interaction between states having different symmetry types:

$$H^{v-v'} = C^{v-v'} y J_y + C^{v-v'}_{yy} \left[ i J_y, J_z^2 \right] + C^{v-v'}_{yJ} i J_y J^2 + C^{v-v'}_{yK} \left[ i J_y, J_z^4 \right] + C^{v-v'}_{yJ} \left[ i J_y, J_z^2 J_z^2 \right] + C^{v-v'}_{yK}$$

114