

Latyshev G.V., Ermilov A.Yu. Modeling of a solvent influence on the oscillation spectrum of hydrogen sulfide

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Modeling of the solvent-solute system is one of the most important problems of the theoretical chemistry. In the present study, an application of some traditional model of a solvent for a description of oscillation spectra of aqueous hydrogen sulfide solutions is discussed. Free H₂S molecule is characterized by three oscillation frequencies (2627.5, 2614.6 and 1182.7 cm⁻¹) [1], corresponding to the anti-symmetric, symmetric, and deformational modes, respectively. A shift of the frequency of the valent oscillation into the red region (about 21 cm⁻¹) is observed in the spectra of combinational dissipation of aqueous hydrogen sulfide [2]. According to experimental data and our calculations of intensities of CD lines, this line can be related to the symmetric valent oscillation.

There are numerous models for solvent applied for the description of different characteristics of a solute and using different approaches. We reviewed an applicability of the common approaches to the description of shifts of oscillation spectra of H₂S molecule. We considered the Onsager's model of reaction field (SCRf), polarization of continuum (PCM), molecular modeling (MM), as well as its variant in the approach of the effective fragment potential (EFP). Results of calculations critically depend on the nature of a solvent.

Calculation procedure and solvent models.

In all the cases, the hydrogen sulfide molecule was described by quantum-mechanical methods, whereas the surrounding was described by a combination of classic and quantum approaches in dependence on the model level. An equilibrium geometric configuration and harmonic frequencies of oscillations of the isolated H₂S molecule were calculated in the Hurtry-Fock approximation with the subsequent analysis of the results, regarding a second-level correlation of the second order of perturbation theory. The correlation corrected atomic basis aug-cc-pVDZ[3] structure[5s4p2d] (sulfur) and [3s2p] (hydrogen), which allows reproduction of three frequencies of the molecule with a close error. The length of the SH bond is overestimated only by 0.003 Å, angle HSH is overestimated only by 2.1° in comparison with the experimental data [1].

The Onsager's model of the reaction field (SCRf) [4, 5] is the simplest method to account for the surrounding. In this model, the molecule is placed into the hypothetical sphere of radius R, whereas the continuous media of the dielectric permittivity ϵ is situated beyond this sphere. Mathematically, it is expressed in addition to Hamiltonian function of an addend $-g\mu^2/2$, where μ is a dipole moment of the molecule, $g = (\epsilon - 1)/(2\epsilon + 1)R^3$ – the Onsager's factor. The iteration method of determination of consistent values for energy and dipole moment was applied. Energy minimization in SCRf results in the increase of the dipole moment in comparison to the isolated molecule. That usually correlated with an "elongation" of bonds and a decrease of their strength. Therefore, it is not unusual (see Table), that frequencies of all oscillations are displaced into the red region, i.e. are lower than the fre-

quencies of the single molecule. Shifts of frequencies are shown for $R = 1.8 \text{ \AA}$, according to the procedure [6].

The model of polarization of continuum [7] (PCM) is a more accurate method of considering the solvent as a continuous media. In this model, the shape of cavity is similar to that of the molecule (as a superposition of Van-der-Waals atomic radiuses). The potential of media is calculated as an electrostatic potential of induced surface charges, which appear at the interface of media with different dielectric permittivity. The scheme of calculation is iterative as well, being performed in every point of the interface.

The molecular modeling is one of the discrete models. In this model, an object for calculation is associates of the initial molecule with the finite amount of solvent molecules. Water molecules are calculated by quantum-chemical methods. We have chosen a level of approximation, which is similar to that of the initial H₂S molecule with the atomic basis [4s3p2d] (aug-cc-pVDZ). The most important, and definitive at large amount of molecules, is choosing an initial geometric configuration of such associate, since an amount of isomers with close energy is huge and demands careful analysis. We took into account a similarity of H₂S and H₂O, and a crystalline structure of ice was taken as a basis. In one of water molecules in a separate cluster (H₂O)_{n+1}, oxygen is being replaced by sulfur. As we assumed, the optimization of the geometry did not change the structural type.

The method of the effective fragment potential [8] (EFP) is based on the replacement of the solvent molecule by a specially matched potential, obtained from the quantum calculation. The constant part of this potential is a combination of fields of point charges, dipoles, quadrupoles, and octupoles, centered on the atoms of the molecule and determined from the analysis of its electron density. Analogously, polarizability of the molecule is a combination of the point polarizabilities of atoms. In order to avoid a "sticking", the repulsive potential is added to each atom. This potential describes the energy at short distance. The method is slightly more difficult for calculation than a calculation of the initial isolated molecule because of the optimization of a position and orientation of the fragments.

The above methods of quantum-mechanical calculations and the solvent models are included into the PC GAMESS computer program [9]. This program was used for calculations.

Discussion. Values for the shifts of the oscillation frequencies of hydrogen sulfide in aqueous solution estimated using different models are shown in Table. The quantitative difference of the results obtained from the models of the continuous (SCRf, PCM) and the structured (MM, EFP) media. Despite the significant difference between the SCRf and the PCM schemes, the results point to the shift of all oscillation frequencies to the red (decrease) side. In our opinion, this effect is related to regarding of polarizability of the solvent only. This results in exceeding of the dipole moment of the system and weakening of bonds. In contrast, in both models of the structured media, the deformational frequency is displaced to the blue side. Exceeding the deformational frequency in liquid water comparatively to vapor counts in favor of these results. In fact, a system of hydrogen bonds makes difficult to distort a valent angle HSH, that results in an increase of this frequency in a solution. A qualitatively correct behavior of the oscillation frequencies is repro-

duced for all complexes (type A), where the hydrogen bonds H-S-H \cdots OH₂ are present, including complexes with one water molecule. In complexes of type B with hydro-

gen bonds H-S-H \cdots SH₂, the shift values are appreciably lower, where its character resembles the results of modeling of solvation of a continuous media.

Table. Variation of oscillation frequencies for H₂S molecule regarding the solvation in different methods

Model	δ , cm ⁻¹	ν_s , cm ⁻¹	ν_{as} , cm ⁻¹
Gas	1182.7	2614.6	2627.5
Gas	1293.5	2846.4	2859.5
models of the continuous media			
SCRF	-18.6	-29.5	-30.3
PCM	-23.7	-10.5	-8.8
models of the discrete media			
1 H ₂ O(A)	+6.70	-5.7	-2.5
1 H ₂ O ^{eff}	+8.5	-8.4	-3.3
1 H ₂ O(B)	-0.3	-1.7	-1.4
1 H ₂ O ^{eff}	-1.1	-2.0	-2.1
2 H ₂ O(A)	+10.2	-6.1	-5.2
2 H ₂ O ^{eff} (A)	+13.7	-8.3	-8.4
2 H ₂ O(B)	-0.9	-2.9	-2.7
2 H ₂ O ^{eff} (B)	-2.3	-3.7	-3.7
4 H ₂ O	+12.0	-18.7	-19.8
4 H ₂ O ^{eff}	+18.1	-26.0	-27.9
12 H ₂ O ^{eff}	+33.5	-45.5	-47.5
38 H ₂ O ^{eff}	+20.8	-19.1	-17.9

Note: *- experiment [1], ** - the SSP method, scaling factory is equal 0.9173

Results of calculation of molecular associates H₂S·nH₂O (n = 1, 2, 4) are reproduced almost ideally in the EFP approach, if water molecules are replaced by the effective fragments H₂S·nH₂O^{eff}. In the most cases, deviations in estimation of the geometric configuration is below 0.01 Å by lengths of valent bonds, 1° for valent angles, and 3 cm⁻¹ for oscillation frequencies. Along with less computation, the EFP method allows significant increase of model systems up to H₂S·38H₂O^{eff}. A quantitative consistency with experiment is observed for cluster with four water molecules. The most perspective method is a modeling of the nearest surrounding using the common cluster approach with addition of the effective fragments.

Conclusion. In the present study, the oscillation spectra of combinational dissipation of aqueous H₂S solutions are described on the basis of quantum-chemical calculation of a molecule in combination with different models of solvation. The Onsager's model of reaction field (SCRF), polarization of continuum (PCM), molecular modeling (MM), as well as a its variant in the approach of the effective fragment potential (EFP) were applied for the description of solvation. The results critically depend on the discrete nature of the solvent. In models of the continuous non-structurized media (SCRF, PCM), frequencies of all oscillations of hydrogen sulfide are displaced to the red region at wide variation of parameters. Regarding of the discrete structure of the solvent allows description of hydrogen bonds and reproduction of an increase of the frequency of deformational oscillation in the solution even for the simplest associates H₂S·nH₂O. A good consistency of calculated values with the experimental shift of the frequency of the valent oscillation of hydrogen sulfide (21 cm⁻¹) is observed for H₂S·4H₂O complex. Modeling of solvent molecules using the effective potential (EFP) perfectly reproduces non-empirical calculations of associates H₂S·nH₂O (n = 1, 2, 4). The above approach gives a real-

istic description of structures with n = 12, 38 and seems to be a perspective method regarding less computation.

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