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Global variational calculations of high-resolution rovibrational spectra: isotopic effects, intensity anomalies and experimental confirmations for H_2S, HDS, D_2S molecules

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Abstract

Variational calculations of high-resolution infrared molecular spectra for isotopically substituted triatomic molecules from potential and dipole moment functions are discussed. A study of intensity anomalies and of their isotopical behavior especially for symmetry-breaking substitutions represents a particularly interesting subject. Extreme manifestations of intensity anomalies present in spectra of the hydrogen sulfide molecule are considered. A first qualitative experimental confirmation of reported theoretical results for deuterium containing species is discussed. ***To cite this article: Vl.G. Tyuterev et al., C. R. Physique 5 (2004).***
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Résumé

Calculs globaux variationnels de spectres rovibrationnels à haute résolution : effets isotopiques, anomalies d'intensités et confirmations expérimentales pour les molécules H_2S, HDS, D_2S. Les calculs variationnels de spectres moléculaires infrarouge à haute résolution, à partir des fonctions potentielle et moment dipolaire pour les molécules triatomiques isotopotomers, sont discutés. Une étude des anomalies d' intensités et de leur comportement isotopique spécialement pour les substitutions qui change la symétrie, présentent un sujet particulièrement intéressant. Des manifestations importantes d'anomalies d'intensité attendues dans les spectres de sulfure d'hydrogène sont envisagées. Une première confirmation expérimentale qualitative des résultats théoriques pour les espèces deutérées est illustrée dans cet article. ***Pour citer cet article : Vl.G. Tyuterev et al., C. R. Physique 5 (2004).***
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Keywords: Variational calculations; Spectra; Intensity anomalies; Isotopic effects

Mots-clés : Calcul variationnel ; Spectres ; Anomalies d'intensités ; Effets isotopiques

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1. Introduction: global rovibrational calculation for molecular isotopic species

Many new atmospheric, astrophysical, and technological applications require an extension of spectral and temperature intervals, more accurate modeling, and reliable isotopic predictions of high-resolution rovibrational molecular spectra. This gives motivations to further improve methods of calculations. Methods which enable one to calculate an entire set of rovibrational states and transitions up to the dissociation from the molecular properties are often refered to in spectroscopy as 'global' methods. A potential energy surface (PES) together with a kinetic operator T is used to calculate energies, wavefunctions and line positions, whereas dipole moment surfaces (DMS) are used to calculate transition probabilities and line intensities. There exist various implementations of these methods. A common feature is a numerical solution of the quantum mechanical eigenvalue problem for the Hamiltonian depending on $3N - 3$ suitably chosen rovibrational coordinates. A variational approach (see [1–5] and references therein) with basis optimization and matix truncation-compression technique is usually applied. A discrete variable representation (DVR) [6] and filter-digitalization [7] techniques aimed at improvement of a basis convergence for high-energy range are also widely used.

Global methods offer complementary possibilities as compared to traditional band-by-band or polyad-by-polyad effective Hamiltonian and effective transition moment models. A comparison of specific advantages and problems of these two approaches in molecular spectroscopy have been recently discussed in [8]. The conceptual simplicity of global spectra prediction for isotopically substituted modifications represents one of the major advantages particularly for non-trivial cases of a symmetry breakdown and also an important test for a validity of the underlying theory. A scheme which illustrates a global approach to rovibrational spectra calculations of isotopic species in a given non-degenerate electronic state is shown in Fig. 1.

Within the Born-Oppenheimer (BO) approximation PES and DMS are isotopically invariant, the kinetic energy operator T for triatomic molecules being exactly defined [1,2,5]. This remains still valid for some higher-order contributions beyond BO approximation such as core correlations and relativistic corrections [9–11]. An isotopic substitution requires then just a
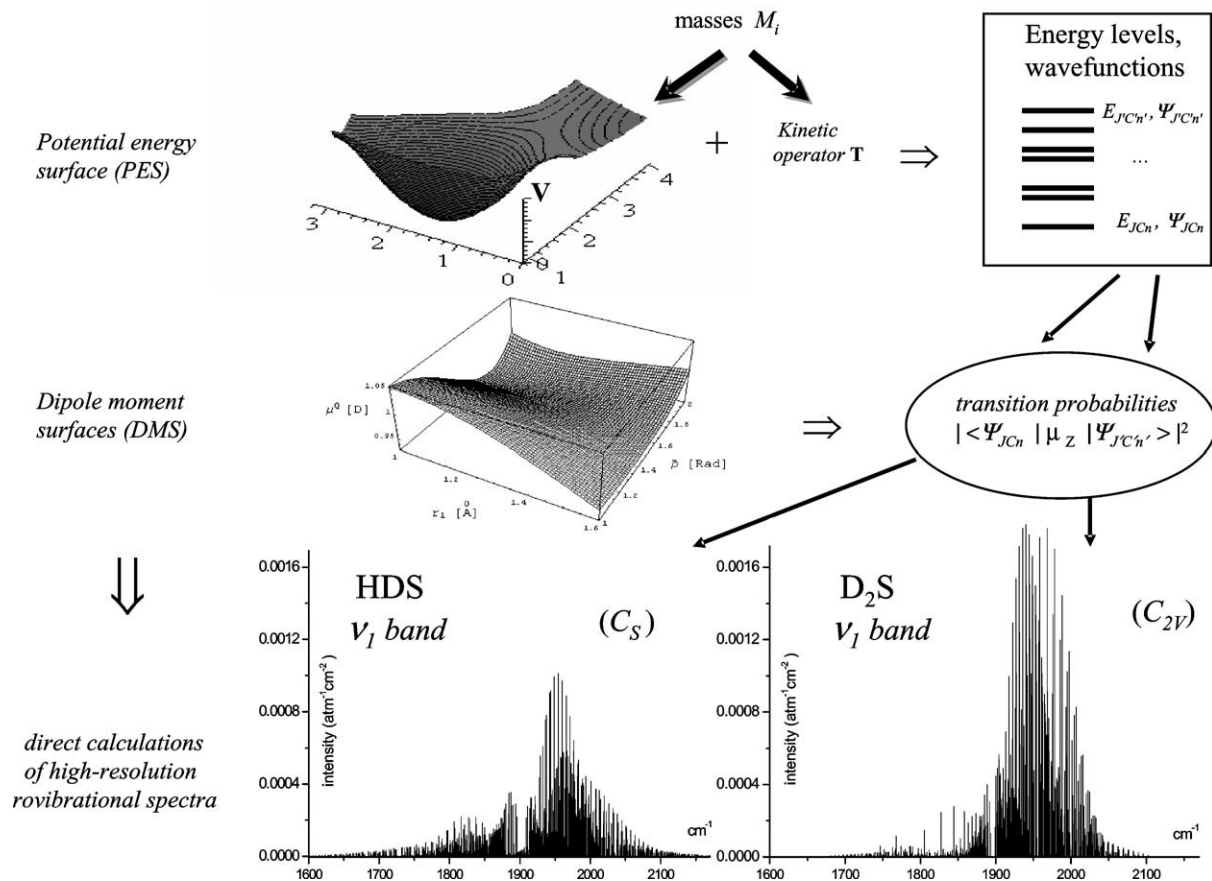

Fig. 1. Scheme of global calculations of high-resolution spectra with isotopic substitutions: example of the ν_1 band of H_2S/HDS molecules at 296 K (the bend-stretch cut for the PES from [18] and for the μ^Q DMS-component from [21])

simple change of mass input values in T, keeping the subsequent computational procedure little changed, contrary to the effective Hamiltonian approach which uses mass dependent normal coordinates and requires a complicated re-definition of parameterizations and different perturbational considerations. However, a very detailed and accurate knowledge of molecular properties (PES, DMS) is needed for their applications to high-resolution spectroscopy. Accurate potential and dipole moment functions have been recently determined for several triatomics such as for example water [10,12,11], ozone [13–16] and H_2S [17–21] either through large ab initio calculations or using extensive empirical optimizations. At a higher level of the theory a separation of electronic states results in mass-dependent corrections $\Delta V(M_i)$ to the PES (whose major contributions are called 'diagonal BO corrections') [9,10,17] and also non-adiabatic corrections ΔT^{NA} to the kinetic energy operator [22,23].

During recent years global variational calculations have reached the accuracy which becomes really useful for analyses of high-resolution spectra of triatomics and this has considerably changed the situation in that domain. In particular this is the case of the spectroscopy of high rovibrational states of the water vapor after global calculations [10,12] based on extensive ab initio determination of PES and DMS combined with subsequent empirical optimization using line position up to $J \leqslant 5$ and including masse dependent contributions to PES for deuterium containing species. The corresponding databank of global predictions [10, 12] containing over 3×10^8 entries is widely used in many recent studies for assignment of weak lines recorded at long optical path [24–26], in hot temperature laboratory and sun-spot spectra [27] and for a confirmation of the line identification in isotopic spectra [28–30]. A review of recent studies can be found in [31].

Another example is related to the isotopic global predictions for the ozone molecule. The analysis the ^{18}O enriched isotopic spectra [32] with a line density ~ 200–300 lines/cm^{-1} is crucially dependent on accurate predictions of 'dark' states and of resonance partners. Calculations using an empirically determined PES [13–15] were found useful for the band and isotopic assignments of dense and complicated ^{18}O enriched spectra containing overlapping bands of six ozone isotopomers simultaneously and have assisted an assignment of over 30 new bands ([32] and references therein). Information on global calculations and molecular properties (PES, DMS, vibrational energy levels up to the dissociation for $^{16}O_3$ and up to 5000 cm^{-1}, $V_{max} = 5$, for all ^{18}O enriched isotopic species is available in the web accessible information system S&MPO (Spectroscopy and Molecular Properties of Ozone http://ozone.univ-reims.fr, http://ozone.iao.ru) [33]. Note that a recent analysis of wave function nodes [34] calculated from ab initio PES [16] has indicated that non-trivial features could appear in assignments of vibration states for C_s isotopomers that has partly been confirmed by the behavior of wave functions obtained from an empirical PES [15] as well.

2. Intensity anomalies: example of the hydrogen sulfide molecule

Line intensity is known to be among most important spectral parameters for various atmospheric applications as it is directly related to analyses of atmospheric gases concentrations. Intensity irregularities and anomalies have been noticed in spectra of many molecules and this is a serious problem in correct modeling of atmospheric transmittance and for minority concentration analyses. Here we shall briefly consider an extreme manifestation of intensity anomalies which were experimentally found in spectra of the hydrogen sulfide molecule ([35,20] and references therein):

(1) observed intensities of H_2S stretching fundamental bands ($\Delta v = 1$) are much weaker than those of combination bands with $\Delta v = 2$, the ν_3 band being particularly weak;
(2) there exists an unusually pronounced asymmetry between branches of certain B-type bands ('suppression' of P-branches);
(3) anomalous rotational distribution (with respect to $\Delta K = 0$ and $\Delta K = 2$ transitions) has been observed in the ν_3 band.

Until recently theoretical attempts to explain anomalies from ab initio calculations and to obtain an agreement of non-empirical calculations with the observations had no success. Ab initio global calculations [36] resulted in an overestimation of the fundamental ν_3 band intensity by an order of magnitude. Moreover, the rotational line intensity distribution in the ν_3 band was in a dramatic disagreement with the observed spectra (in particular the shape of the Q-branch was wrong). On the other hand, ab initio values of the first dipole moment derivatives were in a large disagreement with empirically determined derivatives.

A recent ab initio study [19,20] of DMS has shown that a description of intensity anomalies requires much more accurate determination of molecular properties. The functions of the dipole moment components are extremely shallow in the vicinity of the equilibrium configurations leading to anomalously weak ν_3 and ν_1 bands in the infrared absorption spectrum. This behavior makes the calculation of rovibrational intensities extremely sensitive to small errors in the DMS determination and much more demanding than for other H_2X triatomic molecules. A comparison of the DMS slopes [20] and corresponding intensity predictions clearly shows that even a small error in a DMS variation versus internuclear distance of $\sim 10^{-2}$ Debye/Å can produce a huge overestimation in the intensity calculations for the ν_3 band. This should be one of the major reasons for drastic disagreements of previous ab initio calculations of H_2S intensities with the experimental spectroscopic data. Also, this

makes it necessary to revise [37] the traditional scheme of empirical determination of the dipole moment derivatives using effective models and the perturbation theory.

In this work we focus on the study of the manifestation of intensity anomalies in spectra of deuterium enriched species HDS and D_2S relying on global rovibrational predictions. Though no quantitative experimental measurements of line intensities of HDS and D_2S are available in the literature we are looking for qualitative experimental confirmation through preliminary comparisons with experimental FTS records currently in progress in the University of Reims (see the Section 3).

2.1. Potential energy surface

Advanced program realizations of the global methods allow one to converge rovibrational basis quite well: rather low errors of numerical energy calculations of ~ 0.01–0.001 cm^{-1} are achieved in the best cases. However, a typical accuracy of ab initio PES determination is at present much worse, in the case of H_2S the error reported in [17] is ~ 10–30 cm^{-1} for high vibration states. This suggests an optimization of molecular properties using a least-squares fit of PES parameters using experimental values of line positions and intensities. Such an optimization appears to be much more complicated compared to a fit of conventional spectroscopic parameters in effective models. This is because PES should show a physically meaningful behavior at the entire set of geometrical configurations and should be consistent with the properties obtained from other types of experiments in chemistry, kinetics, etc. (dissociation limits, asymptotics, barriers).

Recent improvement of the global modeling of O_3 and H_2S spectra was due to empirical optimizations of PES using flexible constrains [13,14,18] which play the role of 'penalty functions' for the least-squares fit in a case of non-physical behavior of the fitted surfaces. For this purpose a qualitative behavior of PES checked in each iteration of least-squares fit at a dense grid of geometrical configurations. This allows one to reject those gradients in the parameter space which would drive to a non-physical PES behavior at configurations not sampled by available spectroscopic data, to avoid spurious minima ('holes') and prevent a non-realistic asymptotic and to achieve a better fit helping to overcome some barriers for RMS deviation in a multidimensional parameter space. A combination of various priorities for such constrains provides a possibility for a user guided least-square fitting. The hydrogen sulfide PES obtained in this way has been reported in [18]. A total of 4175 rovibrational energy levels with $J_{max} = 15$, $K_{a\,max} = 15$ for 7 isotopomers (H_2 ^{32}S, H_2 ^{33}S, H_2 ^{34}S, D_2 ^{32}S, D_2 ^{34}S, $HD^{32}S$, and $HD^{34}S$) have been used in the fit. The root-mean-square (RMS) deviation of the rovibrational fit was 0.05 cm^{-1}. For the entire set of all 73 band centres of all isotopic species for which experimental data exists, the RMS deviation of the results of calculations with a single isotopic invariant potential function was 0.03 cm^{-1}. The accuracy of these rovibrational calculations suggests that the isotopically invariant PES obtained in this optimisation was an effective one and should incorporate implicitly some non-Born-Oppenheimer contributions. However, for this molecule we did not find some trends in obs-calc residuals explicitly indicating a necessity to include in the model mass-dependent corrections to the potential function or non-adiabatic contribution to the kinetic energy, at least for this level of accuracy. An example of line position errors for 3341 observed ν_1 transition of HDS is given in Fig. 2.
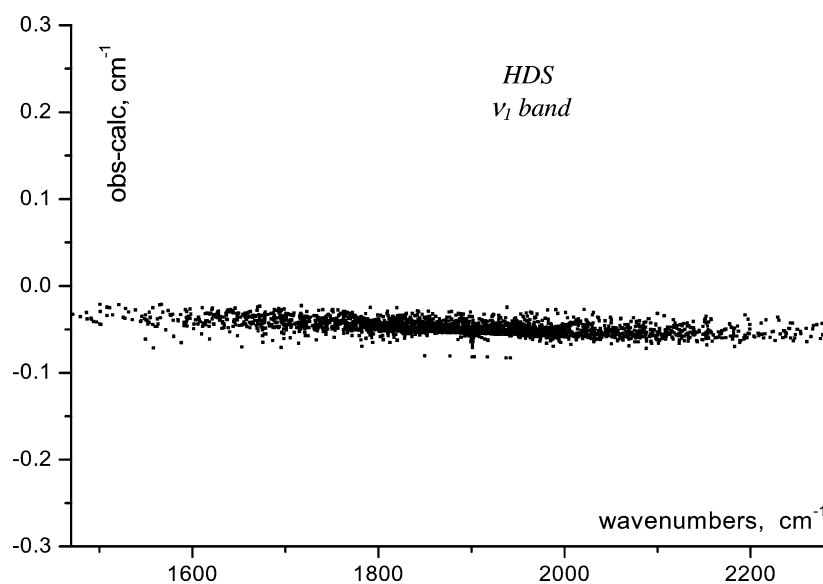

Fig. 2. Example of line position errors for HDS global calculations with PES of [18]. N lines $= 3341$, mean deviation $= -0.048$ cm^{-1}, dispersion (St.dev.) $= 0.008$ cm^{-1}.

2.2. Dipole moment functions

The new ab initio DMS of [19,20] describes well principal vibrational and rovibrational intensity anomalies of the major isotopic species $H_2{}^{32}S$ at least for the fundamentals and $\Delta v = 2$ bands. An empirical optimization of this DMS has been recently achieved [21] including in the fit selected line intensities for low J-values up to $J \leqslant 3$ for fundamental, two-quanta and some three-quanta bands of the major isotopomer $H_2{}^{32}S$ only. Non-resolved doublet and transitions to local-mode near-lying clusters have been excluded from the fit. The resulting optimized dipole moment function contains 34 symmetric component μ^Q parameters following the apex angle bisector axes and 19 asymmetric component μ^P parameters following the orthogonal axes in the molecular plane [21].

2.3. Global isotopic predictions

A large-scale calculations with the above mentioned optimized PES and DMS for rovibrational energy levels, wave functions and transition probabilities (see the scheme of Fig. 1) have been performed using the vector-supercomputer NEC-5X at IDRIS computer center of CNRS (Orsay). We use the exact kinetic energy operator and employ the method and computer code described in [4,10]. A detailed description of calculations, coordinates and basis choice and parameterization is beyond the scope of the paper and is discussed elsewhere [21]. Based on available comparisons for other molecules, we believe that our calculations are converged to better than $0.01\ \mathrm{cm}^{-1}$ for line positions in the considered wavenumber range and to 1–3% in intensities for strong and medium lines and to $\sim 10\%$ for weak lines for room temperature conditions. For the major isotopomer $H_2{}^{32}S$, the intensity results agree well with known experimental measurements as is seen in the example of Table 1 for integrated rovibrational band intensities S_I of the first triad bands obtained by a direct summation of over 7900 lines for $J \leqslant 18$. The discrepancy is of 3% only for the ν_1 band and less than 1% for the ν_3 band which is known to exhibit very pronounced intensity anomalies [20,35,36].

To our knowledge no experimental line intensity measurements on deuterium containing isotopomers HDS and D_2S have been reported in the spectroscopic literature so far. For this reason we were not able to make any empirical dipole moment optimizations relative to deuterium containing isotopomers, and thus calculated intensities for HDS and D_2S are to be considered as non-trivial extrapolations via molecular properties. These global predictions show a series of interesting isotopic intensity effects particularly in appearance of P-, Q- and R-branches, as illustrated in Figs. 1 and 3. Note that the previous theoretical study [38] which used the dipole moment function of [36] produced very different results.

In order to check these isotopic intensity extrapolations and to validate the underlying theory and dipole moment [21] and potential energy [18] functions, a project of experimental studies of related high-resolution spectra in the infrared has been recently initiated in GSMA laboratory of the University of Reims [39]. To prepare analyses of these spectra actually in progress we have generated two theoretical databases of line positions and intensities for the isotopic species of the hydrogen sulphide molecule.

The database_1 includes pure theoretical line positions and intensities generated in the spirit of the scheme of Fig. 1 for the following sample:

- 9 isotopic species: $H_2S/D_2S/HDS$ with ^{32}S, ^{33}S, and ^{34}S substitutions;
- spectral interval: 0–8000 cm^{-1};
- $J_{\max},\ K_{a\,\max} = 18$;
- intensity cut-off $I \leqslant 10^{-27}\ \mathrm{cm}^{-1}/(\mathrm{molecule} \times \mathrm{cm}^{-2})$;
- N (bands) = 135, N (lines) = 420 000.

Assignment of calculated data in terms of normal and local mode vibration quantum numbers and J, Ka, Kc rotational quantum numbers has been carried out [18] to match global (JCn) and spectroscopic notations.

Table 1
Comparison of integrated band intensities calculated from DMS with empirical ones. All intensities are in units $10^{-20}\ \mathrm{cm}^{-1}/(\mathrm{molecule\ cm}^{-2})$

$H_2{}^{32}S$ bands	Empirical S_I [35]	Our calculated S_I	N lines	Our/Empirical
ν_1	1.82	1.87	2632	1.03
ν_3	0.484	0.485	2909	1.00
$2\nu_2$	1.34	1.19	2419	0.89

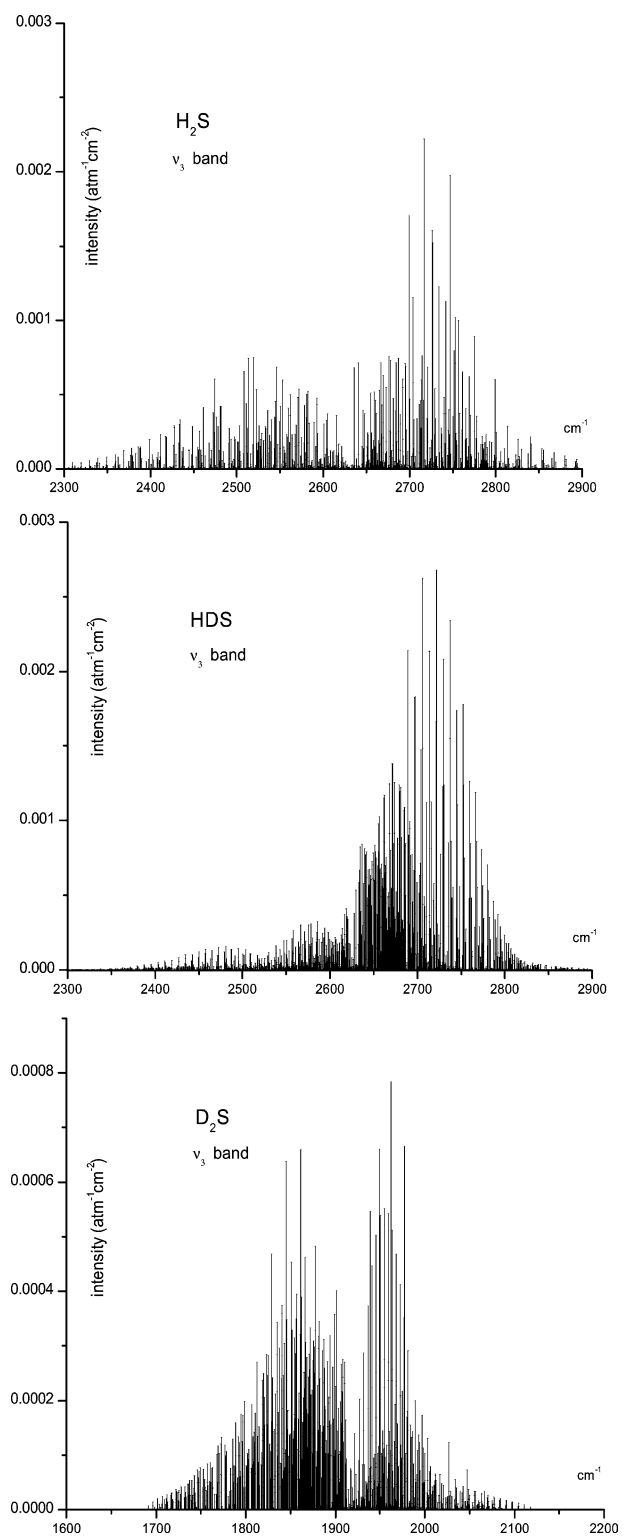Fig. 3. Effect of isotopic substitutions on stick intensity diagrams of the ν_3 band for H_2S, HDS and D_2S molecules in units $atm^{-1}\,cm^{-2}$ at 296 K. Calculated with the PES of [18] and DMS of [21].

The database_2 has the same characteristics as the first one but includes 'empirically calibrated' line positions.

This procedure means the following. If an experimental rovibrational energy level is available in the spectroscopic literature, it was used to replace the corresponding calculated level in the database_1. If it is not that case, but the corresponding experimental vibrational band centre is available, the theoretical level is replaced by $E = E_{\text{glob}} + \Delta v$, where $\Delta v = E_{v\_\text{obs}} - E_{v\_\text{glob}}$ is the error of global calculation for this band centre. The latter procedure is justified by the fact that calculated line positions are in many cases rather homogeneously shifted with respect to observed ones as is seen in the example of Fig. 1. This is because a major error comes from a band centre uncertainty at least for low and medium J values. If no experimental information is available for a band, the energy level is kept as is. Then line positions of the database are regenerated with these corrections. No corrections are applied to line intensities which are the same (issued from global calculations) for both databases.

3. Experimental confirmations

High-resolution infrared spectra of deuterium containing isotopomers of hydrogen sulphide have been recorded [39] in the 800–6000 cm^{-1} range with the Fourier Transform spectrometer built in Reims, the characteristics of the FTS being the same as
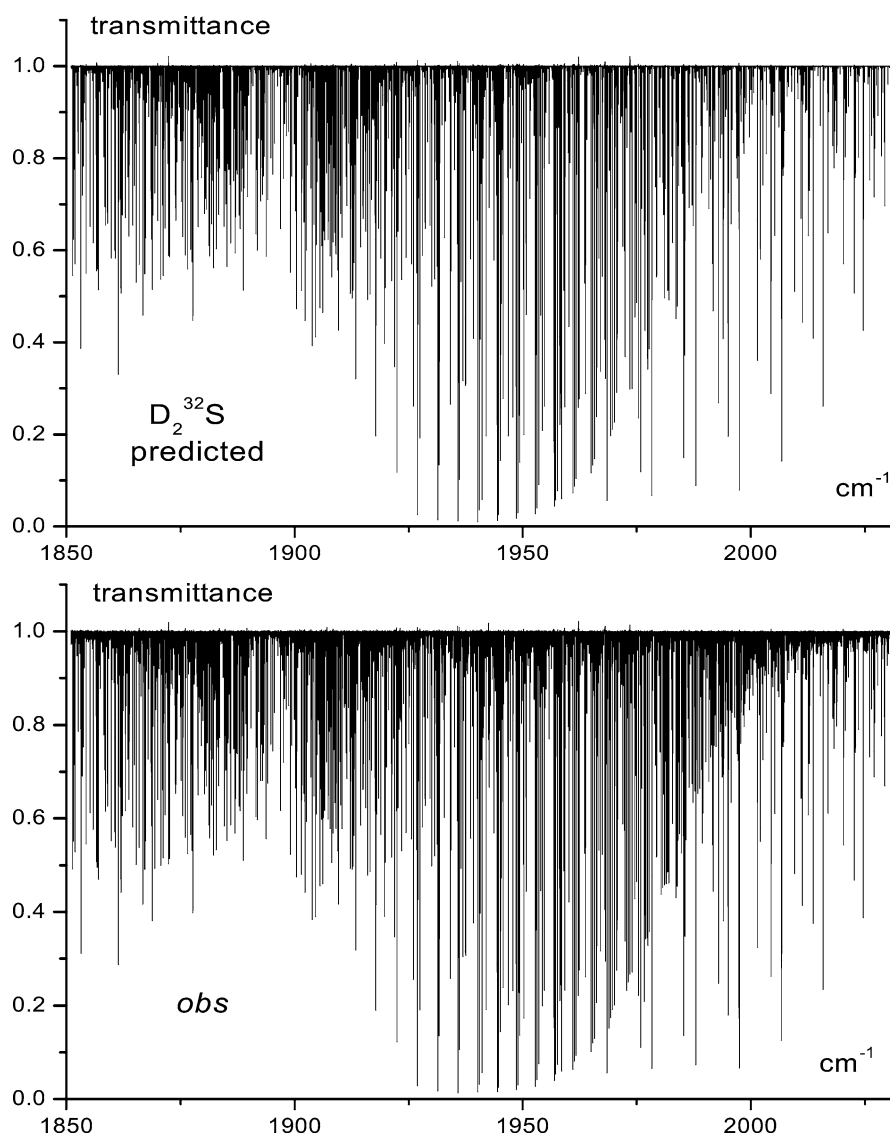

Fig. 4. Large interval comparison of theoretical transmittance simulations near 1900 cm^{-1} using database_1 predictions without empirical corrections (see the text) and the experimental record (32 m optical path, 3.5 Torr of $\sim$95% D$_2$S) at 296 K.
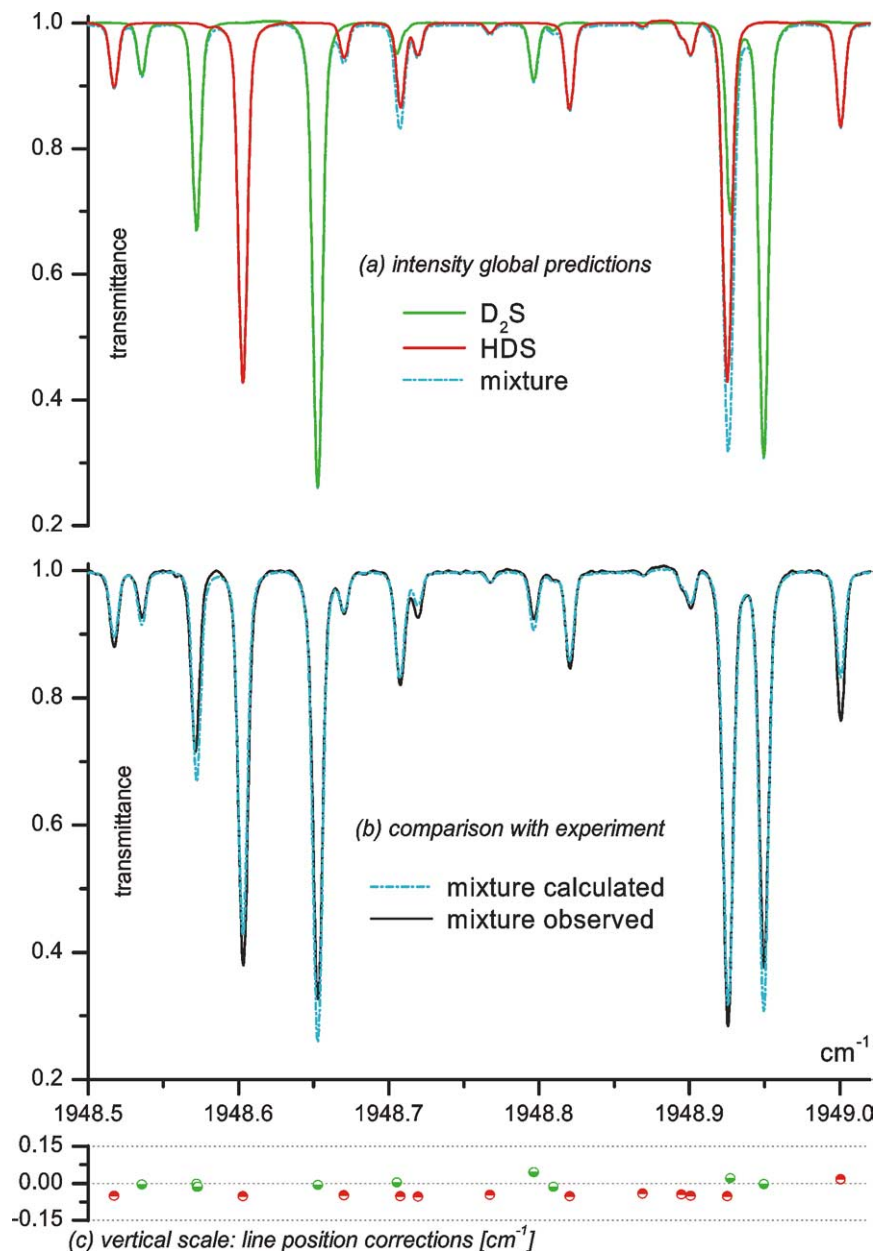
Fig. 5. Narrow interval comparison of theoretical transmittance simulations using the database_2 (see text) and the experimental record (32 m optical path, 2 Torr (H_2S) + 2 Torr (D_2S) in the initial mixture sample) at 296 K. For 31 experimentally visible lines of ν_1, ν_3, $\nu_1 + \nu_2 - \nu_2$ bands of D_2S and ν_1, $2\nu_2$ bands of HDS the mean and RMS deviations for position correction are -0.01 cm^{-1} and 0.03 cm^{-1}, panel (c).

for previously published spectra of ozone and other atmospheric components [32,40] (and references therein). At present we are able to do qualitative comparisons only, because of a difficulty of a precise control of partial pressures of chemically inseparable components in the cell for a mixture of deuterated species (this was possibly the reason of a lack in intensity measurements for HDS and D_2S in the literature).

A comparison between theory and observations is easier for D_2S because we have some records with relatively low abundance of H-containing molecules in the sample. First, overall 'bird's-eye' view comparisons have been carried out in relatively large spectral intervals where impurities do not obscure seriously the picture. At this scale the pure theoretical database_1 is used and the simulation of absorption spectra is made using the Multifit code [40] in the direct calculation mode. An example given in Fig. 4 shows a good agreement with the observed record in the 1900 cm^{-1} range (lower panel with

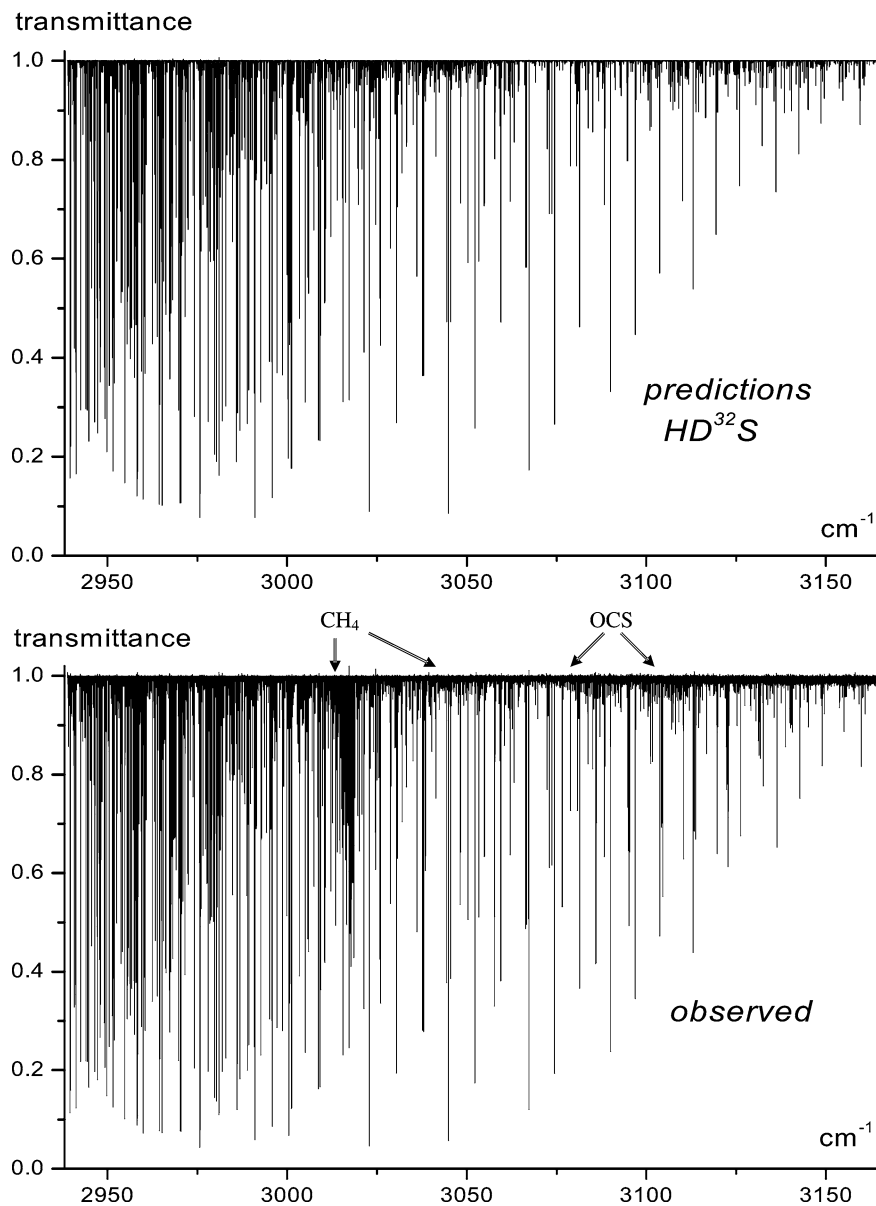Fig. 6. Large interval comparison of theoretical transmittance simulations near 3000 cm^{-1} using database_1 predictions without empirical corrections (see the text) and the experimental record (estimated partial pressure ∼0.89 Torr HDS at 32 m optical path) at 296 K.

about 95% D_2S in the sample). Over 7000 calculated $D_2{}^{32}S$ lines belonging to v_1, v_3, $v_1 + v_2 - v_2$, $v_2 + v_3 - v_2$ bands with a cut-off of 2.5×10^{-8} atm^{-1} cm^{-2} have been accounted for in the transmittance simulation. No empirical corrections have been applied in a large-interval comparison. A line density looks slightly higher in the observed spectrum because of remaining deuterated water and other impurities present in the cell.

A comparison for a mixture of deuterated species is given in Fig. 5. At narrow interval scales it was found more convenient to use the database_2, because this allows separating more clearly uncertainties in intensity predictions (panels (a), (b) of Fig. 5) and line position errors (lower panel (c) of Fig. 5) and correctly visualizing overlapping lines with D_2S and HDS absorption contributions.

It was not possible to prepare a pure HDS sample but there are some large-interval comparisons where HDS provides a dominant contribution as is seen in Fig. 6 at the 3000 cm^{-1} range. As in Fig. 4 no empirical corrections were used in the upper panel simulation, including about 2500 lines of the database_1 belonging mostly to v_3, $3v_2$ and $v_1 + v_2$ HDS bands. Again
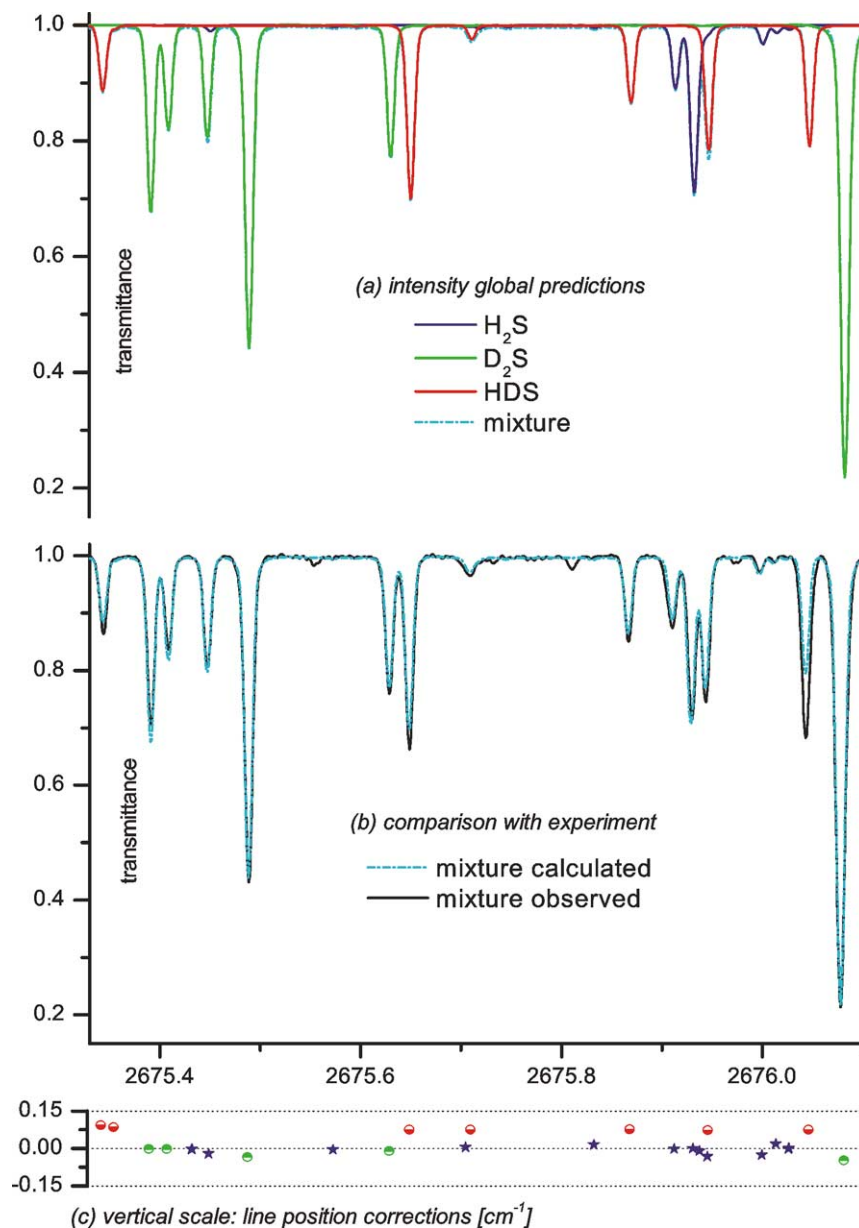
Fig. 7. Narrow interval comparison of theoretical transmittance simulations using the database_2 and the experimental record with simultaneous H_2S, HDS and D_2S absorption (see text) at 296 K.

the absorption is slightly underestimated, which is partly explained by impurities in the cell (CH_4, OSC, ...) but a qualitative agreement looks very good.

Fig. 7 shows an interval near 2675 cm^{-1} were all three species H_2S, HDS and D_2S contribute to the absorption. A sample was prepared with initial 2 Torr (H_2S) + 2 Torr (D_2S) with a preliminary estimation of 0.89 Torr (HDS) in a final mixture. Notations and the calculation procedure are the same as in Fig. 5. The residual discrepancies in HDS line intensities can partly be due to the uncertainty in a partial pressure determination in the sample.

4. Conclusion

To summarize, we believe that a large number of lines involved in the above validations suggest that reported predictions for isotopic variations of spectra are qualitatively well confirmed for the considered frequency range. Theoretical predictions

previously available in the literature are in a large disagreement with our data. Analyses of experimental spectra, accurate partial pressure calibrations and intensity measurements are currently in progress [39]. An extension of measurements to a high frequency range would be of interest. A theoretical challenge would be to rationalize the above isotopic intensity variations in terms of traditional effective models based on a perturbation theory.

Acknowledgements

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