Recent advances in global variational and effective calculations of the line positions and intensities for triatomic molecules: some features of a new generation of spectroscopic databanks

VI.G. Tyuterev

University of Reims, France

Theoretical methods currently used for calculations and modeling of line position and intensities for rovibrational transitions in high-resolution molecular spectra are briefly reviewed. Problems related to an accurate description of bands corresponding to large ΔV, to high rovibrational states and intensity anomalies are illustrated with examples for isotopic species of $\hat{I}_3$, H_2S, and $\hat{I}_2\hat{I}$ molecules. Some features of a new generation of spectroscopic databanks, which contain information on potential/dipole moment functions and global predictions are discussed.

Introduction

The HITRAN, GEISA, and GPL[1–3] databases of spectroscopic line parameters that are widely used in atmospheric applications contain both experimental data and results of theoretical modeling. For many molecules calculated data represent a major part of line positions and intensities currently included in databases. In particular, this is the case with overlapping bands, hot spectra, weak transitions, and also of some heavy molecules, for which accurate measurements of intensities and of line-width for entire spectra are hardly possible because of the blended or non-resolved structures. Thus, for the ozone molecule as an example important for atmospheric applications, nearly all line parameters in the infra-red included in compilations[1,2] are calculated. Most of the specialized databanks/software packages like TDS[4] and STDS[4] for methane and other spherical tops contain calculated data only.

Many new atmospheric, astrophysical, and technological applications require an extension of spectral and temperature intervals, more accurate modeling, and reliable isotopic predictions. This gives motivation to further improving the methods of calculations and to develop complementary theoretical tools. This paper is based on the review talk at the ASA-2002 workshop where some recent tendencies and problems related to global and effective calculations for high-resolution spectroscopy and for atmospheric applications have been discussed.

During recent five years global "first principles" variational calculations have reached the accuracy, which becomes really useful for analyses of high-resolution spectra of triatomics (see, for example, Refs. 6 to 9 and references therein) and this has considerably changed the situation in the domain. These new possibilities of calculating and modeling spectra have been supported by a progress in informatics, numerical algorithms and by the development of methods for non-linear optimization of molecular properties (MP). Related global predictions and information on MP are included in the new generation of spectroscopic databanks and information systems (see Refs. 6, 7, and 10 to 12).

Here we give a brief comparison of theoretical methods and related new features of databanks with illustrations for spectra of O_3, H_2S, H_2O molecules and their isotopomers, which are of a particular concern at high vibrational states, intensity anomalies and high J, K_a transitions (Table 1). The examples are based on recent studies of GSMA (Reims) in collaboration with IOA (Tomsk) and Aims Center (NASA).

Table 1. "Input and output" information in global (variational) calculations for spectroscopic applications

Molecular properties (MP)	⇔	Spectroscopic/chemical information
Potential functions (PES)	⇔	Rovibrational line positions, dissociation path
Dipole moment functions (DMS)	⇔	Transition probabilities, line intensities
Wave functions	⇔	Assignments of high states, normal-to-local transitions, bifurcation analysis,...
Primary interest	⇔	High-energy states, hot bands, weak bands, "dark"-state perturbations, isotopic predictions

Examples of databanks containing MP and spectra predictions based on MP		
Molecule	Specific problem	Databank
Water	problems for high rotational states	Refs. 6, 47
Ozone	Vibrational state problem near dissociation	Refs. 10–12
$H_2S/D_2S/HDS$	Intensity anomalies	Ref. 78

1. Main theoretical approaches

Among various methods and theoretical models for calculation of high-resolution molecular spectra (HRMS) three most widespread types are to be considered:

(i) *"local" (effective) methods*, based on the perturbation theory and on effective Hamiltonians for sets of nearby vibrational states (polyads) accounting for strong rovibrational resonance interactions within these polyads;

(ii) *"intermediate" version of calculations*, which use vibration extrapolation scheme for successive polyads;

(iii) *"global" methods* (many of them use a *variational* technique) which enable one to calculate an entire set of rovibrational (RV) states and transitions up to the dissociation and even above from the molecular properties; a potential energy surface (PES) is used to calculate energies and line positions and dipole moment surfaces (DMS) are used to calculate line and band intensities.

A scheme which illustrates these approaches is shown in Fig. 1.

Until recently "local" effective models (i) have been most widely used in high-resolution spectroscopy because these allow a good accuracy for low and medium quantum numbers to be achieved using relatively simple computations. These models are usually derived by applying Contact Transformations (CT)[13–16] or alternative forms of the perturbation theory to simplify the full rovibrational Hamiltonian. This provides a mathematical background for intuitively introduced physical models for bound states of semi-rigid molecules near the equilibrium configuration and makes it possible to give a simple interpretation of the low-order parameters. The major advantage of the methods (i) is that this approach allows one to reduce an extent of calculations by focusing on a certain group of vibrational states "localized" within a limited energy interval. The latter is supposed to be of interest for an interpretation of a concrete experimental spectrum within a given wave number range. In this sense we refer to these models as to "local" ones (independent of whether normal or local coordinates are used in calculations). Thus the dimension of matrices is dramatically reduced and computational realization becomes much simpler. Consequently a metrological accuracy of calculations is feasible, but relatively large number of phenomenological parameters is required to characterize each polyad separately. For asymmetric top molecules a well-known example is the Watson's model for effective centrifugal distortion Hamiltonian and its extensions.[17,18] This-type models are widely used to calculate line parameters and to fill spectroscopic databases in series of works by Flaud, Camy-Peyret and co-workers[19,20] and of many other research groups (see, for instance Refs. 21 and 22 and references therein).

Apart from a large total number of parameters difficult to evaluate theoretically, the main problem of these "local" models is extrapolation of empirical information to other spectral intervals and also to other isotopic species. The related difficulties are most strongly pronounced for highly excited rovibrational states and in particular for nonrigid molecules.
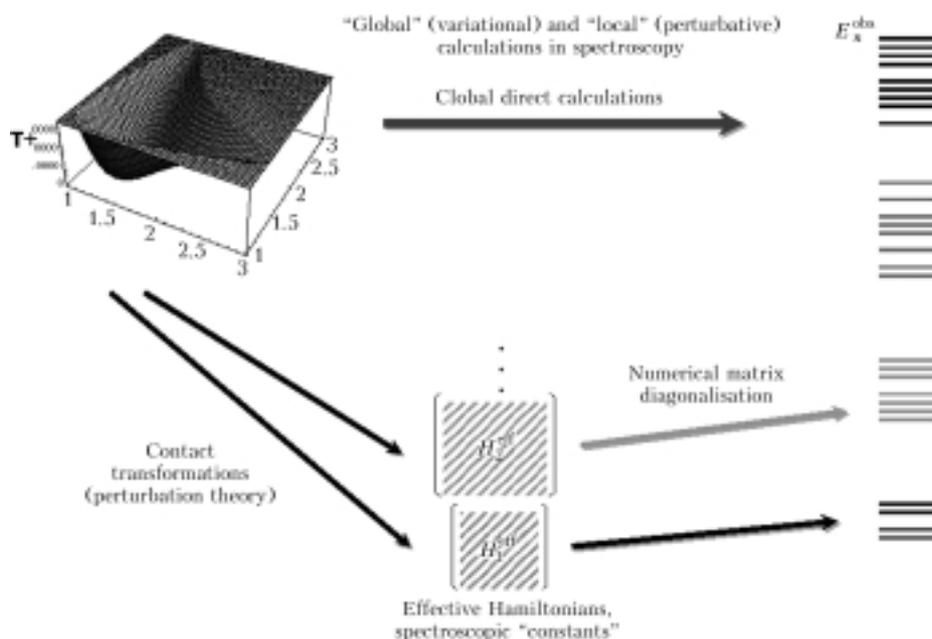

Fig. 1. Approaches (i), (ii) and (iii) for a calculation of molecular rovibrational levels (see Sect. 1 for definitions).

In these cases simple zero-order models (harmonic oscillators, normal modes, and rigid rotor) are no more justified physically because the corresponding states observed are beyond the domain of convergence of the standard perturbation expansion. To improve the convergence of the expansion of the perturbation theory, new non-polynomial models for effective Hamiltonians have been developed for nonrigid H_2O type molecules. The *generating function model*[23-25] and the *four-dimensional bending-rotation model*[26-27] allow improvement of the accuracy in the fit of rovibrational data and extrapolations to higher J, K_a. A detailed review of recent studies in this domain is given in Ref. 28.

"Intermediate" models (ii) are also based on the perturbation theory and effective Hamiltonians for closely neighboring (localized) groups of vibrational states, but this approach aims at relating parameters of successive polyads. This allows extrapolations for energies and line positions to be made, thus partly compensating for the drawback of "local" models. The related advantage is more difficult (or even impossible) to realize for intensity extrapolations to larger ΔV. However, the intensity extrapolations proved to be quite efficient for certain series of hot bands. Vibration extrapolation models (ii) are currently employed for spherical top molecules (Champion and co-workers,[29] LPUB Dijon) using irreducible tensors formalism that has been successively extended to symmetric top molecules by Nikitin et al.[30-32] and applied to accurate analyses of CH_3D spectra. A specialized program package MIRS[32] has been recently developed for this purpose. A vibration extrapolation approach (ii) has allowed a considerable progress in modeling of spectra of linear molecules (Tashkun, Perevalov and co-workers[33,34] (IOA, Tomsk), and Teffo (LPMA, Paris[35])). These calculations have been used to generate specialized, TDS and SDTS, databanks for methane and spherical tops[4,5] and a high temperature bank CDSD for CO_2.[36] Note that above mentioned specific constraints of the perturbation theory equally apply to the approach (ii). In particular, a high accuracy of calculations has been achieved in those cases where the nontrivial part of the V-dependence of matrix elements is sufficiently smooth and can be approximated by polynomials. The latter is valid for semi-rigid molecules in the domain of the applicability of normal vibration modes that is far below the dissociation limit.

A detailed discussion of effective models (i) and (ii) and extended reference list is given in the review papers 14, 37, and 38. Some mathematical aspects of the problem in relation to the properties and dynamics of Hamiltonian systems have been considered in Ref. 39.

"Global" methods (iii) contrary to the previous approaches (i) and (ii) are not limited by constraints of the perturbation theory. Thus, they are expected to better describe higher states. However a very detailed and accurate knowledge of molecular properties (PES, DMS) is needed for their applications to high-resolution spectroscopy. Information on non-adiabatic interactions is necessary in some cases. There exist various implementations of methods (iii). A common feature is numerical solving of the quantum mechanical eigenvalue problem for the Hamiltonian depending on $3N-3$ rovibrational coordinates. A variational approach is usually applied. Studies of Carter, Handy, Light, Carrington, Jensen, Wattson, Rothman, Tennison, Satcliff, Schwenke, Rosmus and co-workers (see for example Refs. 40 to 47 and references therein) as well as of many groups working on applications of quantum chemistry to spectroscopy have contributed to a spectacular recent development of this approach for triatomic molecules. Some examples of global calculations in high-resolution spectroscopy based on recent studies of GSMA (Reims) in collaboration with IOA (Tomsk) and NASA (Aims Center) are given in Sections 2–5. A parameterization, optimization, and computer implementation of global methods (iii) are much more complicated than those of "local" models (i) and (ii). At present they do not assure a competitive metrological precision, but are capable of giving a consistent "bird-eye" view on the entire set of all bound rovibrational states and qualitatively reliable predictions. An accurate modeling of PES and DMS is required to achieve this end.

The schematic presentation of input/output information in methods of global calculations is given in Table 1 and Figs. 2, 3. A comparative analysis of advantages and problems for local and global methods summarized in Table 2 suggests that their use in spectroscopy should be complementary.

Table 2. Brief overview of relative advantages of (i)-(iii) methods in HRS applications

Features	Local (perturbational) models	Global (non-perturbational) models
1	2	3
Accuracy of data fit for low V and J	*~ experimental* *=> metrological applications*	*not competitive*
Dimension of the problem in the wavefunction space (matrices)	*finite low dimension* *=> very fast calculations* *=> no basis convergence problems*	*"infinite" dimension* *=> basis convergence problem;* *complications at bound states ⇔ continuum*
Programming:	*relatively easy*	*sophisticated numerical methods needed*
Loss of accuracy of ro-vib lines fit with increasing number of atoms	*excellent accuracy still possible for rotational (MW) and fundamental bands transitions; quite moderate loss in IR with low V*	*accuracy degrade dramatically for N > 3; improvement expected in future*

Table 2 (continued)

| 1	2	3
Physical meaning of parameters	*Low orders => clear* *High orders => nobody cares ?*	*Imposes sever restrictions:* *avoid "holes", assure asymptotic,* *dissociation limit, barrier heights, …*
High *V, J*	*Convergence of perturbation expansions ?* *=> model problems for non-rigid molecules*	*Numerically "exact" (to a certain digital* *position) non-perturbational calculations*
Use of *ab initio* information to evaluate lines for new bands / molecules	*very limited*	*major advantage of the approach*
High energy (dense) states near dissociation	*overlapping of polyads*	*full account of various interactions* *=> information for dynamics*
Prediction from lower polyads => to higher polyads	*limited;* *(better with "intermediate" models =>* *vibrational extrapolations)*	*major interest of models*
Number of parameters with increasing polyads	*explosion*	*smoothly increases*
Completeness of predictions	*limited by certain energy range /* *spectral intervals*	*full database possible for all ro-vibrational* *bound state transitions (light molecules);* *calculations of very high-J transitions for* *heavy molecules difficult due to* *dimension/memory limitations*
Isotopic predictions	*complicated and* *unreliable if symmetry changes*	*very simple (with isotopically invariant* *PES/DMS) and powerful*
Ambiguities/uncertainty of parameterization; lack of information	*(1) correlations (collinearity) of* *parameters => Hamiltonian reduction* *needed for higher orders/polyads;* *(2) "dark" state problem;*	*(1) re-assignment:* *global ⇔ "spectroscopic" quantum numbers;* *(2) problems of effective account for* *adiabatic, non-adiabatic, relativistic* *contributions, etc. in direct or inverse* *calculations*
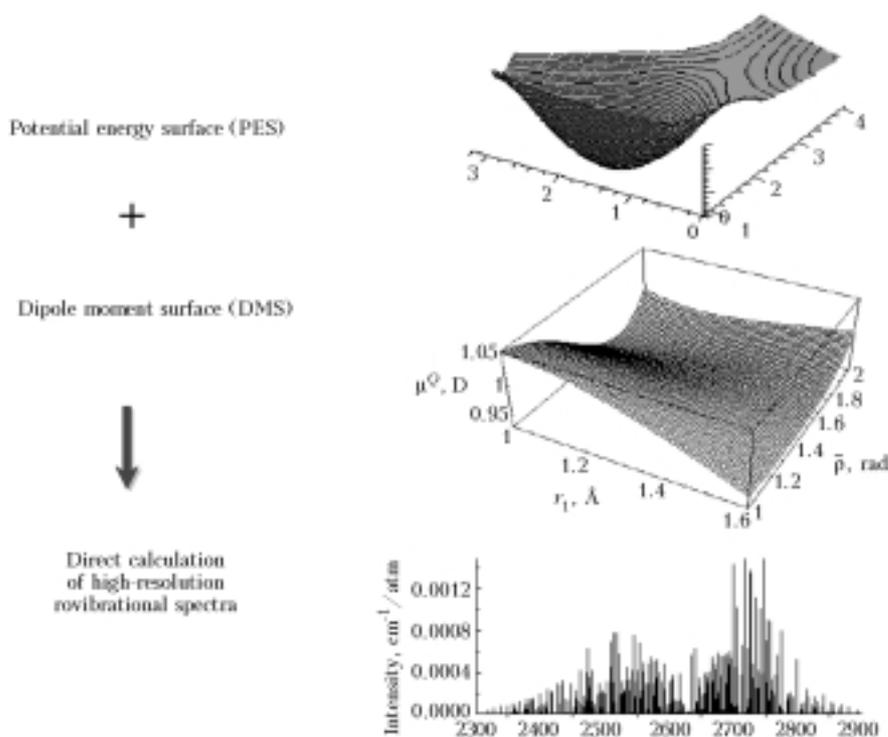
Fig. 2. Scheme of global calculations of high-resolution spectra: example of the H_2S molecule (the bend-stretch cut for the PES from Ref. 50 and for the μ^O DMS-component from Ref. 9; calculated spectrum for the ν_3 band from Ref. 9).
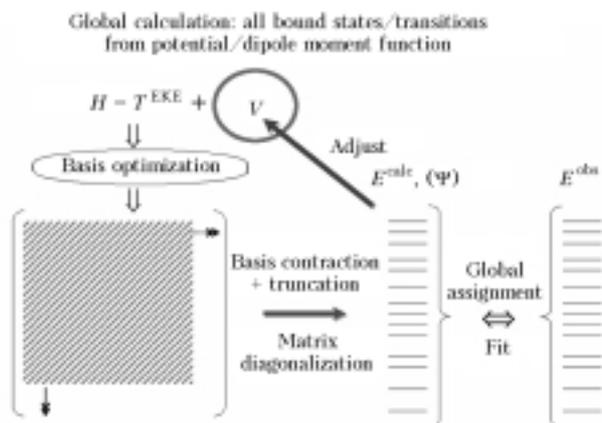
Fig. 3. Successive steps for a potential energy surface (PES) optimization in global calculations (iii) using experimental spectroscopic data.

2. Inverse calculations in global methods: optimization of PES with flexible constraints

Advanced program realizations of the (ii) methods allow one to converge rovibrational basis quite well: rather low errors of numerical energy calculations $\sim 0.01-0.001$ cm^{-1} are achieved in the best cases. However a typical accuracy of *ab initio* PES determination is at present much worse $\sim 10-100$ cm^{-1}. This suggests an optimization of molecular properties using a least-squares fit of PES and DMS 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 (i) and (ii). This is because PES and DMS 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 described in Sect. 4 and 5 was due to new approach in empirical optimization of PES implemented in our work together with Tashkun.[51] This uses flexible constrains 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 and DMS are checked in each iteration of least-squares fit at a dense grid of geometrical configurations (~ 200000 configurations in the case of the ozone PES[49]). 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;

— avoid spurious minima (holes) and prevent a non-realistic asymptotic;

— 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*.

3. H$_2$O: problem of modeling for high rotational states

As mentioned above, non-polynomial effective models (i), such as the *generating function model* [23–25] and the *four-dimensional bending-rotation model*[26–27] allow better convergence and extrapolations compared to the standard perturbation expansions. For medium values of the quantum numbers this gives the RMS deviation of a line position fit $\sim 0.01-0.003$ cm^{-1} of H_2O spectra in the infrared and an order of magnitude better for lower states. For example, all 2350 measured line positions of the 2nd triad spectra recorded at optical path ~ 300 m at pressure ~ 30 mbar have been calculated with the RMS deviation of 0.005 cm^{-1} (Mikhailenko et al.[52,53]) using the generating function model. This extends considerably the domain of applicability of effective Hamiltonians (i) compared to standard models that are polynomials in angular momentum components.

However this domain remains still limited. An accurate extension of "local" models should be particularly difficult to achieve for bending-rotational states beyond the linearity barrier. For a full description of very high excited states observable in hot spectra the global approach is certainly better placed. The situation in spectroscopy of high rovibrational states of the water vapor has drastically changed after global calculations published by Partridge and Schwenke.[6,7] In these studies the high-level *ab initio* calculations of PES and DMS have been combined with subsequent empirical optimization using line position up to $J \leq 5$. This has resulted in the calculated large-scale PS-database[6,7] on predicted high-temperature line parameters of H_2O containing over 3×10^8 entries. Though for certain spectral intervals and quantum numbers this database can show larger discrepancies with observations compared to the best effective calculations (as it is the case of (000), (010) states[24] and first and second triads[27,52,53]), it has many obvious advantages. Thanks to a systematic and self-consistent representation of the entire set of all rovibrational transitions and of the major interactions this allows one to correct many assignment and mistypen errors which had been present in traditional spectroscopic databases (see an example of comparison in Fig. 4).

The databank of global predictions by Partridge and Schwenke is widely used in many recent studies for assignment of weak lines recorded at long optical path,[54,55] in hot temperature laboratory, and sun-spot

spectra[8,56] and for a confirmation of the line identification in isotopic spectra for HDO[57] and $H_2^{18}O$ (Ref. 58, see also discussion in Ref. 59).
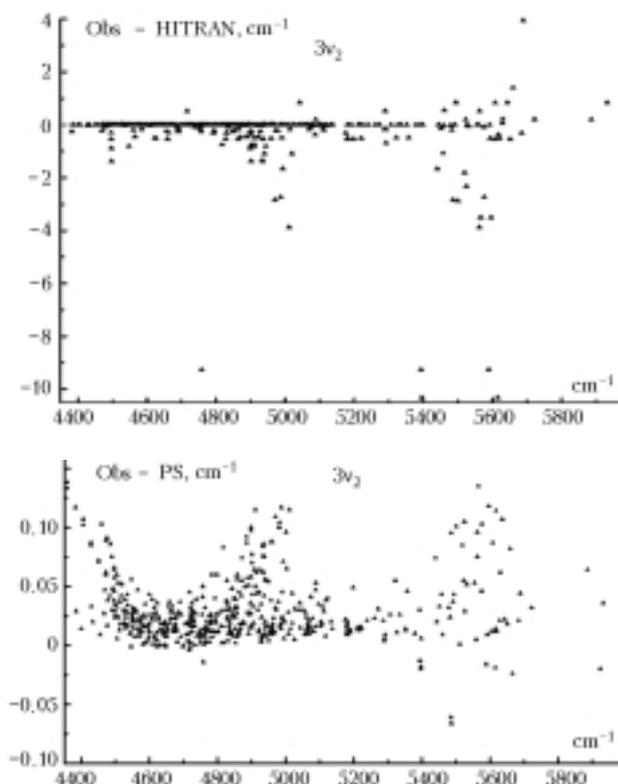

Fig. 4. Comparison of Partridge and Schwenke (PS, Ref. 6) global predictions and of the HITRAN-2000 compilation[1] with the observed H_2O line positions for the $3\nu_3$ band according to Mikhailenko et al., Ref. 53.

4. O_3: high vibration states and isotopically enriched spectra

As mentioned in the introduction, the absolute majority of atmospheric compilations for ozone line parameters in the infrared relies on calculations. This is a consequence of difficulties of systematic line measurements in very dense ozone spectra. For the states far below the dissociation limit the molecule behaves as a rather rigid one. Under these conditions effective models (i) appear to be well adapted for an accurate description of the rovibrational interactions.

Corresponding semi-empirical calculations that use adjusted parameters in effective Hamiltonians and in transition moments provide a precision comparable to the experimental one (see Refs. 19, 20, 22, and 60 to 64): $\Delta\nu \sim 10-100\,kHz$ in the microwave range, $\Delta\sigma \sim 10^{-4}\,cm^{-1}$ for line positions and $\Delta I \sim 2\%$ for line intensities in the best analyses for strong bands in the infrared. The uncertainty progressively increases up to $(1-3) \times 10^{-3}$ for line positions and to $\sim 10-20\%$ for intensities of weak transitions, in particular for high overtones and combination bands. Rather complete line lists based on spectra analyses up to the wave numbers $< 3000-4000\,ñm^{-1}$ performed by Flaud, Camy-Peyret, Rinsland, and other groups (see Refs. 19 and 60) have been included in atmospheric compilations HITRAN and GEISA (Refs. 1, 2, and 60).

More then 20 new ozone bands have been analyzed in a series of studies by Barbe and co-workers.[22,61-63] In particular many new rovibrational line positions and intensities up to $\Delta V \le 6$ have been measured in the range $3000-6000\,ñm^{-1}$ (see recent review by Mikhailenko et al.[64] for more detail and literature references). To correctly model these new experimentally measured spectra, it was necessary to account for various multiple resonances $(\nu_1\,\nu_2\,\nu_3) \leftrightarrow \leftrightarrow (\nu'_1\,\nu'_2\,\nu'_3)$. Unusually high-order accidental resonances with very large total variation of vibrational quantum number up to $\Delta V = 8, 9$ were found to be important. This is the case of the resonances $(310) \leftrightarrow (041)$, $(401) \leftrightarrow (024)$, $(123) \leftrightarrow (330)$, $(015) \leftrightarrow (080)$, and so on (see Ref. 64).

An account of these resonances results in an overlap of classical stretching ozone polyads and complicates the analysis. In the frame of effective methods (i) information on new interaction parameters can hardly be obtained from previously analyzed bands. Extended polyads contain many "dark" states. The latter are not directly observable under normal experimental conditions but can perturb observed states.

Information on the entire set of ozone vibration states can be obtained from global predictions (iii) that require accurate potential functions. In Refs. 48 and 49 the effective ground electronic state PES of the $^{16}O_3$ molecule has been obtained in a least squares fit to the largest sample of experimental, high-resolution data used for this purpose so far. All vibrational data available from HRMS experiments up to $\Delta V \le 6$ in the wave number range up to $5600\,cm^{-1}$ have been included in the PES optimization using flexible constraints as described in Sect. 2. The average accuracy of calculations from the potential function for 85 centers of known cold and hot bands was $0.08\,cm^{-1}$. The rovibrational energy levels of 26 low-lying vibrational states up to $J = 5$ were also included with the RMS deviation of $0.02\,cm^{-1}$. Rotational extrapolation tests $J = 5 \rightarrow \rightarrow J = 10$ have demonstrated the predictive power of the PES (the extrapolation error $\sim 0.06\,cm^{-1}$ rarely achievable in global calculations). Very high-excited "dark" states and "stretching levels" experimentally determined by the dissociative Raman spectroscopy (Chang et al.[65]) were not included in our fit but were calculated in extrapolation up to the dissociation limit within their experimental accuracy (RMS = $1.6\,cm^{-1}$).

A reliable evaluation of the ozone PES by non-empirical methods has become possible only recently: the first global *ab initio* PES of the ozone has been published by Siebert, Schinke, et al.[66] in 2002. A root-mean-square deviation of the *ab initio*

calculations was $RMS_{vib} \sim 5$ cm^{-1}. Though *ab initio* PES is less accurate then the empirical PES (see Refs. 48 and 49) near the open equilibrium configuration, *ab initio* calculations from Ref. 66 have allowed the potential function for those nuclear configurations to be determined, which are not accessible via current spectroscopic experiments (ring ozone structure).

Ab initio calculations[66,67] have confirmed a physically meaningful behavior of the spectroscopically determined PES[48,49] at qualitatively important limits. Both PESs show the dissociation barrier (a controversial question actually under discussion), and give an excellent agreement with the experimental value of D_0. The agreement in equilibrium configurations for the open ozone structure and for the diatomic fragment and the agreement at linearity barriers and in the energy of a simultaneous breaking of two O−O bonds are also very good.

Another important issue is related to the isotopic global predictions. According to experimental estimations by Barbe et al.,[68] the line density in the ^{18}O enriched isotopic spectra is ~ 200 lines/cm^{-1}. The analysis is then crucially dependent on accurate predictions of "dark" states and of resonance partners. In recent study[69] a following step in the PES optimization has been undertaken using simultaneous fit to experimental data of various isotopic modifications of the ozone molecule. The average accuracy of vibrational calculations for all measured bands for 668, 686, 688, 868, and 888 species[70–72] up to 5600 cm^{-1}, and also for known bands of ^{17}O enriched species 667, 676 (Ref. 20) is $RMS_{vib} \sim 0.02$ cm^{-1} in with this latest PES version.[69]

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 (Fig. 5)) is available in the specialized information system S&MPO (Spectroscopy and Molecular Properties of Ozone) developed in collaboration between GSMA (University of Reims) and LTS IAO (Tomsk).[10–12]
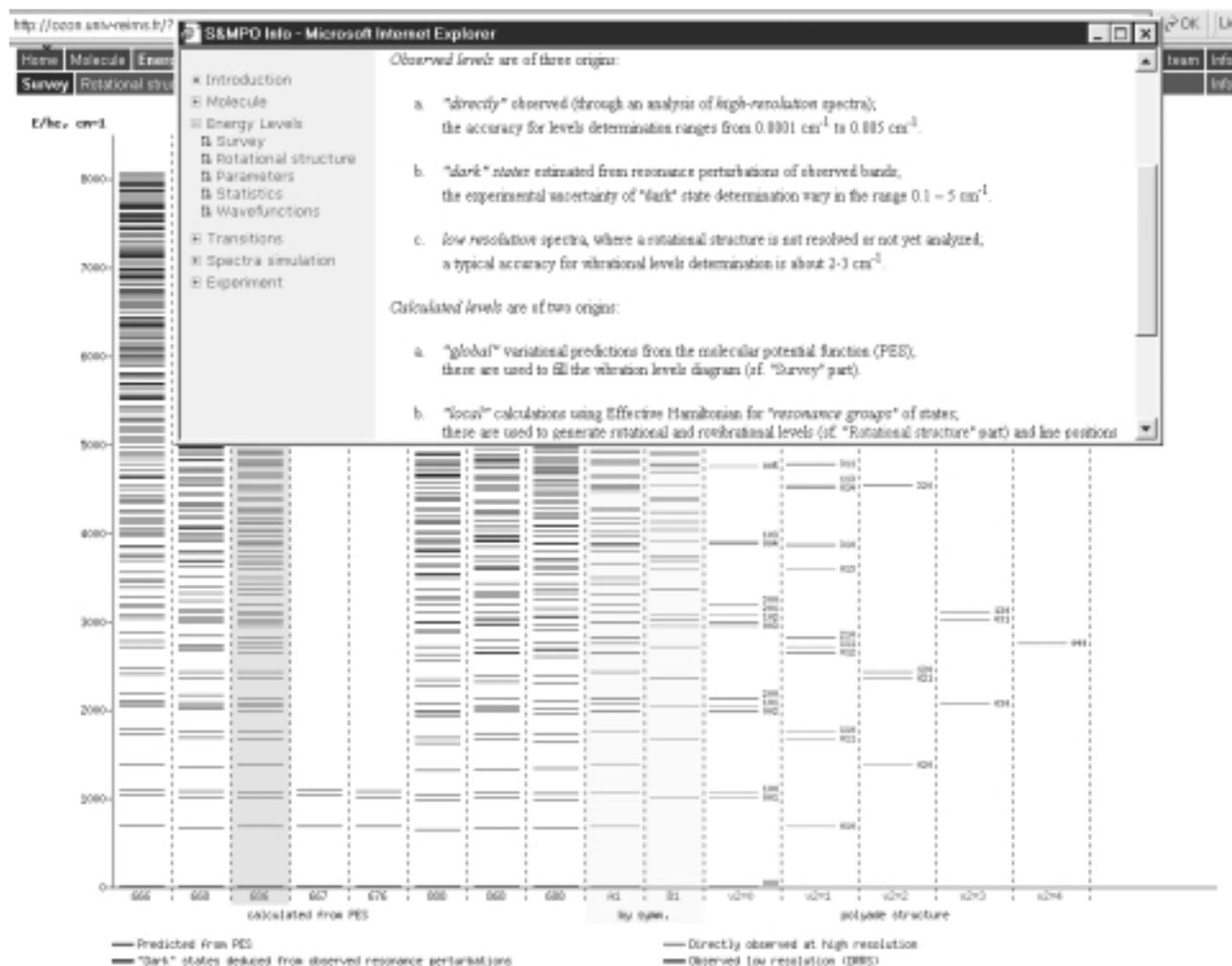

Fig. 5. Global calculations for isotopic vibrational levels of ozone in the S&MPO information system (Refs. 10 to 12) (GSMA, Reims & LTS, Tomsk). For the $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, and $^{16}O^{18}O^{18}O$ species (corresponding abbreviations 668, 686, 868, and 688) the isotopically invariant PES of Ref. 69 has been used for calculations and assignments.

S&MPO includes also most recent calculations of rovibrational spectra using "local" effective models (i), parameters for resonance groups, and experimental FTS spectra recorded in Reims. It contains a database of line parameters which is more complete than that of HITRAN and GEISA in the range $3000-6000$ cm^{-1}. The S&MPO system is Internet accessible (at two equivalent sites http://ozone.univ-reims.fr and http://ozone.iao.ru) and offers various user-friendly interactive functions, such as synthetic spectra simulation and their comparison with the experimental records.

5. H₂S/D₂S/HDS: intensity anomalies

Line intensity is known to be among most important spectral parameters for various atmospheric applications as it is directly related to retrievals of atmospheric gas components.

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 retrievals. In this Section we shall briefly consider an extreme manifestation of intensity anomalies which are present in spectra of isotopic modification of the hydrogen sulfide molecule:

(1) observed intensities of H₂S fundamental bands ($\Delta v = 1$) are much weaker than those of combination bands with $\Delta v = 2$, the v_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 v_3 band.

Analyses of experimental spectra have been carried out by Emerson, Lechuga-Fossat et al. and in recent series of studies by Braun, Naumenko, Flaud, Campargue, and co-workers (see Refs. 21, 73, and 74 and references therein).

Theoretical attempts to explain anomalies from *ab initio* calculations and to obtain an agreement of non-empirical calculations with the observations had no success during a rather long time. The HRMS *ab initio* global calculations[75] resulted in an overestimation of the fundamental v_3 band intensity by an order of magnitude. Moreover the rotational line intensity distribution in the v_3 band were 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 new recent analysis of *ab initio* DMS[9] 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 v_3 and v_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 H₂X triatomic molecules. A comparison of the DMS slopes[9] and corresponding intensity predictions clearly shows that even a small error in a DMS variation versus internuclear distance $\sim 10^{-2}$ Debye/Å can produce a huge overestimation in the intensity calculations for the v_3 band. It should be one of the major reasons for drastic disagreements of previous *ab initio* calculations of H₂S intensities with the experimental spectroscopic data. Also, this makes it necessary to revise[76] the traditional scheme of empirical determination of the dipole moment derivatives using effective methods (i). The new *ab initio* DMS[9] describes well principal vibrational and rovibrational H₂S intensity anomalies known so far (Figs. 6 and 7).
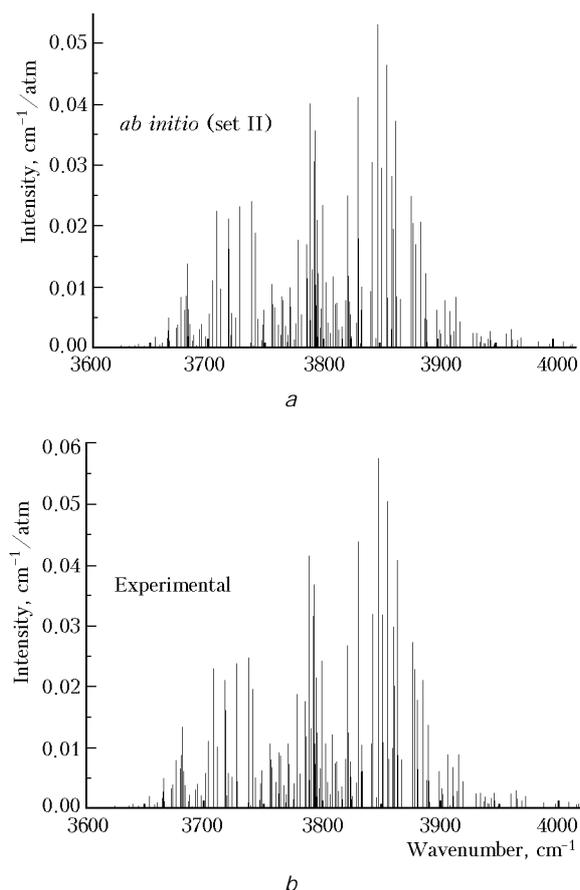

a

b

Fig. 6. The stick spectrum of the $v_2 + v_3$ band of H₂S: comparison of *ab initio* (*a*), Ref. 9, and experimental (*b*), (Ref. 21) intensities. The relative error in the integrated band intensity is comparable with the uncertainty of the empirical determination: $(S_{obs} - S_{ab\ initio}) / S_{obs} = 4\%$.
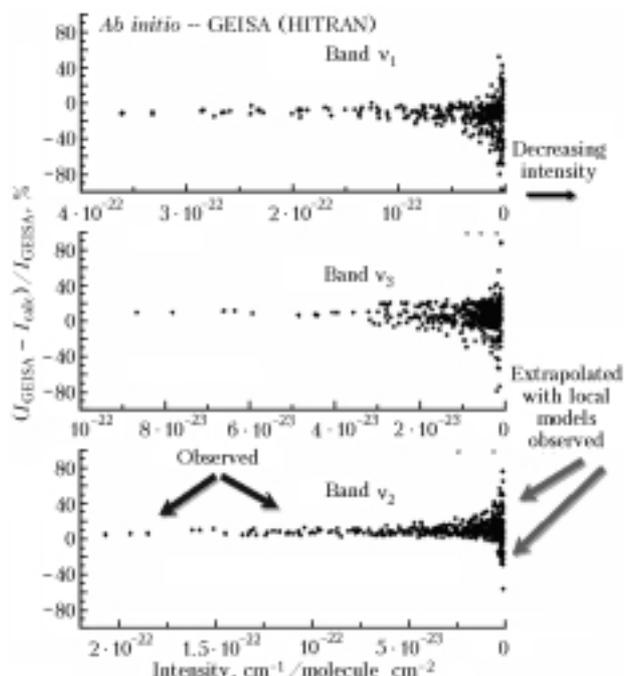
Fig. 7. Comparison of the intensities calculated from the *ab initio* dipole moment function (CRT −surface, Ref. 9) for rovibrational transitions of the 1st H_2S triad with semi-empirical values included in GEISA, HITRAN banks[1,2] of the spectral line parameters.

The next step was an optimization of PES[50] and DMS[77] using experimental data and creation of calculated bank of line position and intensities of various isotopic species of the hydrogen sulfide molecule through the methods of the type (iii). The first preliminary version of such a databank of global spectra calculations has been developed in GSMA (University of Reims) in collaboration with LTS IOA (Tomsk) and contains the following information[78]:

   – 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 $I < 10^{-27}$ cm^{-1}/(moleculexcm^{-2});
   – N (bands) = 135, N (lines) = 420 000.

The calculations have been carried out at IDRIS computer center of CNRS (Orsay). One of the examples of the application of the theoretical study of intensity anomalies to isotopic spectra using dipole moment function is given in Fig. 8.

Acknowledgments

Fig. 8. Comparison of line intensity predictions for D_2S (Ref. 78) with the experimental spectrum recorded later on. Line positions are calculated using the PES from Ref. 50 with subsequent "calibration" against known experimental levels (shift ~0.05 cm^{-1}). D_2S intensities are calculated with the wave functions from Ref. 50 and with DMS from Ref. 77 without empirical corrections specific to D_2S spectra. The observed: FTS of Reims (L.Regalia-Jarlot et al., 2002), $P(D_2S)$ = 5.73 Torr, I = 32.16 m.

References

1. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, and P. Varanasi, *The HITRAN molecular spectroscopic database*, J. Quant. Spectrosc. Radiat. Transfer **60**, 665–710 (1998).

2. N. Jacquinet-Husson, E. Arié, J. Ballard, A. Barbe, G. Bjoraker, B. Bonnet, L.R. Brown, C. Camy-Peyret, J.-P. Champion, A. Chédin, A. Chursin, C. Clerbaux, G. Duxbury, J.-M. Flaud, N. Fourrié, A. Fayt, G. Granier, R. Gamache, A. Goldman, V.I. Golovko, G. Guelachvili, J.M. Hartmann, J.C. Hilico, J. Hillman, G. Lefévre, E. Lellouch, S.N. Mikhailenko, O.V. Naumenko, V. Nemtchinov, D.A. Newnham, A. Nikitin, J. Orphal, A. Perrin, D.C. Reuter, C.P. Rinsland, L. Rosenmann, L.S. Rothman, N.A. Scott, J. Selby, L.N. Sinitsa, J.N. Sirota, A.M. Smith, K.M. Smith, Vl.G. Tyuterev, R.H. Tipping, S. Urban, P. Varanasi, and M. Weber, *The 1997 spectroscopic GEISA databank*, J. Quant. Spectrosc. Radiat. Transfer **62**, 205 (1999).

3. H.M. Pickett, R.L. Poynter, E.A. Cohen, M.L. Delitsky, J.C. Pearson, and H.S.P. Muller, *Submillimeter, millimeter, and microwave spectral line catalog*, J. Quant. Spectrosc. Radiat. Transfer **60**, 883 (1998).

4. Vl.G. Tyuterev, Yu.L. Babikov, S.A. Tashkun, V.I. Perevalov, A. Nikitin, J.-P. Champion, J.C. Hilico, M. Loete, C.L. Pierre, G. Pierre, and Ch. Wenger, *T.D.S. spectroscopic databank for spherical tops*, J. Quant. Spectrosc. Radiat. Transfer **52**, 459–480 (1994).

5. C. Wenger and J.-P. Champion, *Spherical Top Data System (STDS) software for the simulation of spherical top spectra*, J. Quant. Spectrosc. Radiat. Transfer **59**, 471 (1998).

6. H. Partridge and D.W. Schwenke, *The determination of an accurate isotope dependent potential energy surface for water from extensive ab initio calculations and experimental data*, J. Chem. Phys. **106**, 4618–4639 (1997).

7. D.W. Schwenke and H. Partridge, *Convergence testing of the analytical representation of an ab initio DMS function of water: Improved fitting yields improved intensities*, J. Chem. Phys. **113**, 6592–6597 (2000).

8. J. Tennyson, *Computational Molecular Spectroscopy* (J. Wiley&Sons, Chichester, 2000).

9. T. Cours, P. Rosmus, and Vl.G. Tyuterev, *Ab initio dipole moment function of* $H_2^{32}S$ *and intensity anomalies in rovibrational spectra*, J. Chem. Phys. **117**, 5192–5208 (2002).

10. Vl.G. Tyuterev, A. Barbe, S.N. Mikhailenko, and Yu.L. Babikov, *The ozone molecule: S&MPO information system on WEB. State of art in recent studies on molecular properties and high-resolution spectroscopy*, in: *The 17th Colloquium on High Resolution Molecular Spectroscopy*, Nimègue (Sept. 2001).

11. S. Mikhailenko, Yu. Babikov, Vl.G. Tyuterev, and A. Barbe, *The databank of ozone spectroscopy on WEB (S&MPO)*, Computational Technologies **7**, 64–70 (2002), (in Russian).

12. A. Barbe, S.N. Mikhailenko, Vl.G. Tyuterev, Yu.L. Babikov, *The spectral and molecular properties of ozone (S&MPO) databank*, in: *HITRAN Conference*, 2002.

13. G. Amat, H.H. Nielsen, and G. Tarrago, *Rotation-Vibration of Polyatomic Molecules* (Dekker, New York, 1971).

14. M.R. Aliev and J.K.G. Watson, *Higher-order effects in the vibration-rotation spectra of semirigid molecules*, in:

Molecular Spectroscopy: Modern Research (Academic Press, San Diego, CA, 1985), Vol. III, pp. 1–67.

15. Vl.G. Tyuterev and V.I. Perevalov, *Generalized contact transformations for quasi-degenerate levels*, Chem. Phys. Lett. **74**, 494–502 (1980).

16. Yu.S. Makushkin and Vl.G. Tyuterev, *Perturbation methods and effective Hamiltonians*, in: *Molecular Spectroscopy* (Nauka, Novosibirsk, 1984).

17. J.K.G. Watson, *Determination of centrifugal distortion coefficients of asymmetric top molecules*, J. Chem. Phys. **46**, 1935–1949 (1967).

18. J.K.G. Watson, *Vibrational spectra and structure*, Durig. J. Ed. **6** (Elsevier, Amsterdam, 1977), pp. 1–89.

19. J.-M. Flaud, C. Camy-Peyret, C.P. Rinsland, M.A.H. Smith, and V. Malathy Devi, *Atlas of Ozone Line Parameters from Microwave to Medium Infrared* (Academic Press, New York, 1990).

20. J.-M. Flaud and R. Bacis, *The ozone molecule: infrared and microwave spectroscopy*, Spectrochim. Acta **54A**, 3–16 (1998).

21. L.R. Brown, J.A. Crisp, D. Crisp, O.V. Naumenko, M.A. Smirnov, L.N. Sinitsa, and A. Perrin, J. Mol. Spectrosc. **188**, 148 (1998).

22. A. Barbe, J.J. Plateaux, S.N. Mikhailenko, Vl.G. Tyuterev, *Infrared spectrum of ozone in the* 4600 *and* 5300 cm^{-1} *regions: high order accidental resonances through the analysis of* $\nu_1+2\nu_2+3\nu_3-\nu_2$, $\nu_1+2\nu_2+3\nu_3$, *and* $4\nu_1+\nu_3$ *bands*, J. Mol. Spectrosc. **185**, 408–416 (1997).

23. Vl.G. Tyuterev, *The generating function approach to the formulation of the effective rotation Hamiltonian. Simple closed form model describing strong centrifugal distortion in water type molecules*, J. Mol. Spectrosc. **151**, 97–129 (1992).

24. Vl.G. Tyuterev, V.I. Starikov, S.A. Tashkun, and S.N. Mikhailenko, *Calculation of high rotational energies of water molecule using the generation function model*, J. Mol. Spectrosc. **170**, 38–58 (1995).

25. V.I. Starikov and Vl.G. Tyuterev, *Method of intramolecular interaction theory in spectroscopy of nonrigid molecules*, Atmos. Oceanic Opt. **8**, Nos. 1–2, 93–104 (1995).

26. L.H. Coudert, J. Mol. Spectrosc. **154**, 427–442 (1992).

27. R. Lanquetin, L.H. Coudert, and C. Camy-Peyret, *High-lying rotational levels of water: an analysis of the energy levels of the five first vibrational states*, J. Mol. Spectrosc. **206**, 83–103 (2001).

28. V.I. Starikov and Vl.G. Tyuterev, *Intramolecular Ro-Vibrational Interactions and Theoretical Methods in the Spectroscopy of Nonrigid Molecules* (SB RAS, Tomsk, 1997), 230 pp.

29. J.-P. Champion, M. Loete, and G. Pierre, *Spherical top spectra*, in: *Spectroscopy of the Earth's Atmosphere and Interstellar Medium* (Academic Press, San Diego: 1992), pp. 339–422.

30. A. Nikitin, J.-P. Champion, and Vl.G. Tyuterev, *Improved algorithms for the modeling of vibrational polyads of polyatomic molecules: application to* T_d, O_h, *and* C_{3v} *molecules*, J. Mol. Spectrosc. **182**, 72–84 (1997).

31. A. Nikitin, J.-P. Champion, Vl.G. Tyuterev, L.R. Brown, G. Mellau, and M. Lock, *The infrared spectrum of* CH_3D *between* 900 *and* 3200 cm^{-1}, *extended assignment and modeling*, J. Mol. Structure **517–518**. 1–24 (2000).

32. A. Nikitin, J.-P. Champion, and Vl.G. Tyuterev, *The MIRS computer package for modeling the rovibrational spectra of polyatomic molecules*, J. Quant. Spectrosc. Radiat. Transfer, special HITRAN issue, 2003 (to be published).

33. S.A. Tashkun, V.I. Perevalov, J.-L. Teffo, L.S. Rothman, and Vl.G. Tyuterev, *Global fitting of* $^{12}C^{16}O_2$ *vibrational-rotational line positions using the effective Hamiltonian approach*, J. Quant. Spectrosc. Radiat. Transfer **60**, 785−801 (1998).

34. S.A. Tashkun, V.I. Perevalov, J.-L. Teffo, and Vl.G. Tyuterev, *Global fit of* $^{12}C^{16}O_2$ *vibrational-rotational line intensities using the effective operator approach*, J. Quant. Spectrosc. Radiat. Transfer **62**, 571−598 (1999).

35. J.L. Teffo, O.M. Lyulin, V.I. Perevalov, and E.I. Lobodenko, *Application of the effective operator approach to the calculation of* $^{12}C^{16}O_2$ *line intensities*, J. Mol. Spectrosc. **187**, 28−41 (1998).

36. S.A. Tashkun, V.I. Perevalov, J.L. Teffo, A.D. Bykov, and N.N. Lavrent'eva, *CDSD-1000, the high-temperature carbon dioxide spectroscopic databank*, J. Quant. Spectrosc. Radiat. Transfer, special HITRAN issue, 2003 (to be published).

37. K. Sarka and J. Demaison, *Perturbation theory, effective Hamiltonians and force constants*, in: *Computational Molecular Spectroscopy* (J. Wiley, Chichester, 2000).

38. Vl.G. Tyuterev, V.I. Perevalov, and V.I. Starikov, *Method of effective operators in theory of high-resolution molecular spectra*, in: *Modern Problems of Optics and Spectroscopy* (TGU, Tomsk, 2001).

39. Vl.G. Tyuterev, *Effective Hamiltonians and perturbation theory for quantum bound states of nuclear motion in molecules*, in: *Symmetry and Perturbation Theory* (World Scientific Publishing, 2002), pp. 254−266.

40. S.E. Choi and J.C. Light, *Highly excited vibrational eigenstates of nonlinear triatomic molecules. Application to* H_2O, J. Chem. Phys. **97**, 7031−7054 (1992).

41. J.R. Henderson, C.R. Le Sueur, and J. Tennyson, Comput. Phys. Commun. **75**, 379 (1993).

42. M.J. Bramley and T. Carrington, Jr., *A general discrete variable method to calculate vibrational energy levels of three- and four-atom molecules*, J. Chem. Phys. **99**, 8519−8541 (1993).

43. P. Jensen, *New Morse Oscillator-Rigid Bender Internal Dynamics (MORBID) Hamiltonian for triatomic molecules*, J. Mol. Spectrosc. **128**, 478−501 (1988).

44. D.W. Schwenke, *Variational calculations of rovibrational energy levels and transition intensities for tetratomic molecules*, J. Phys. Chem. **100**, 2867−2884 (1996).

45. W. Gabriel, E.-A. Reinsch, P. Rosmus, S. Carter, and N.C. Handy, *Theoretical integrated vibrational band intensities of water vapor*, J. Chem. Phys. **99**, 897 (1993).

46. P. Jensen and P. Bunker, *Computational Molecular Spectroscopy* (J. Wiley&Sons, Chichester, 2000).

47. L.S. Rothman, R.B. Wattson, R.R. Gamache, D. Goorvitch, L.R. Hawkins, and J.E.A. Selby, *HITEMP, the high-temperature molecular spectroscopic database*, J. Quant. Spectrosc. Radiat. Transfer, in preparation.

48. Vl.G. Tyuterev, S.A. Tashkun., P. Jensen, A. Barbe, and T. Cours, *Determination of the effective ground state potential energy function of ozone from high resolution infrared spectra*, J. Mol. Spectrosc. **198**, 57−76 (1999).

49. Vl.G. Tyuterev, S.A. Tashkun, D.W. Schwenke, P. Jensen, T. Cours, A. Barbe, and M. Jacon, *Variational EKE-calculations of rovibrational energies of the ozone molecule from an empirical potential function*, Chem. Phys. Lett. **316**, 271−279 (2000).

50. Vl.G. Tyuterev, S.A. Tashkun, and D.W. Schwenke, *An accurate isotopically invariant potential function of the hydrogen sulfide molecule*, Chem. Phys. Lett. **348**, 223−234 (2001).

51. Vl.G. Tyuterev and S.A. Tashkun, private communication.

52. S.N. Mikhailenko, Vl.G. Tyuterev, K.A. Keppler, B.P. Winnewisser, M. Winnewisser, G. Mellau, S. Klee, and K.N. Rao, J. Mol. Spectrosc. **184**, 330−349 (1997).

53. S.N. Mikhailenko, Vl.G. Tyuterev, V.I. Starikov, K.K. Albert, B.P. Winnewisser, M. Winnewisser, G. Mellau, C. Camy-Peyret, R. Lanquetin, J.-M. Flaud and J.W. Brault, *Water spectra in the* 4200−6250 cm^{-1} *region: extended analysis of* $\nu_1+\nu_2$, $\nu_2+\nu_3$, *and* $3\nu_2$ *bands and confirmation of highly excited states from flame spectra and from atmospheric long-path observations*, J. Mol. Spectrosc. **213**, 91−121 (2002).

54. L.P. Giver, C. Chackerian, Jr., and P. Varanasi, *Visible and near-infrared 161 line intensity corrections for HITRAN-96*, J. Quant. Spectrosc. Radiat. Transfer **66**, 101−105 (2000).

55. M. Carleer, A. Jenouvrier, A.C. Vandaele, P. Bernath, M-F. Mérienne, R. Colin, N.F. Zobov, O.L. Polyansky, J. Tennyson, and V.A. Savin, *The near infrared, visible, and near ultraviolet overtone spectrum of water*, J. Chem. Phys. **111**, 2444−2450 (1999).

56. N.F. Zobov, O.L. Polyansky, J. Tennyson, S.V. Shirin, R. Nassar, T. Hirao, P.F. Bernath, and L. Wallace, *Using laboratory spectroscopy to identify lines in the K- and L-band spectrum of water in a sunspot*, The Astrophysical Journal **530**, 994−998 (2000).

57. O. Naumenko, A. Campargue, E. Bertseva, and D. Schwenke, *Experimental and ab initio Studies of the HDO absorption spectrum in the* 13 165−13 500 cm^{-1} *spectral region*, J. Mol. Spectrosc. **201**, 297−309 (2000).

58. S.N. Mikhailenko, Vl.G. Tyuterev, and G. Mellau, (000) *and* (010) *states of* $H_2^{18}O$: *analysis of rotational transitions in hot emission spectrum in the* 400−850 cm^{-1} *region*, J. Mol. Spectrosc., accepted (2002).

59. A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Water Vapor Spectroscopy* (SB RAS Publishing House, Novosibirsk, 1999), 376 pp.

60. C.P. Rinsland, J.-M. Flaud, A. Perrin, M. Birk, G. Wagner, A. Goldman, A. Barbe, M.-R. De Backer-Barilly, S.N. Mikhailenko, Vl.G. Tyuterev, M.A.H. Smith, V. Malathy Devi, D.C. Benner, F. Schreier, K.V. Chance, J. Orphal, and T.M. Stephen, *Spectroscopic parameters for ozone and its isotopes: recent measurements, outstanding issues, and prospects for improvements to HITRAN*, J. Quant. Spectrosc. Radiat. Transfer, special HITRAN issue, 2003 (to be published).

61. A. Barbe, A. Chichery, Vl.G. Tyuterev, S.A. Tashkun, and S.N. Mikhailenko, *Infrared high-resolution spectra of ozone in the range* 5500−5570 cm^{-1}: *analysis of* $\nu_2+5\nu_3$ *and* $\nu_1+\nu_2+4\nu_3$ *bands*, J. Phys. B: At. Mol. Opt. Phys. **31**, 2559−2569 (1998).

62. A. Barbe, S.N. Mikhailenko, J.J. Plateaux, and Vl.G. Tyuterev, *Analysis of the* $2\nu_1+\nu_2+2\nu_3$ *band of ozone*, J. Mol. Spectrosc. **182**, 333−341, (1997).

63. A. Barbe, A. Chichery, Vl.G. Tyuterev, and J.J. Plateaux, *Analysis of high resolution measurements of the* $\nu_1+5\nu_3$ *band of ozone: Coriolis interactions with the* $6\nu_3$ *and* $3\nu_1+\nu_2+2\nu_3$ *bands*, Molecular Physics **94**, 751−757 (1998).

64. S.N. Mikhailenko, A. Barbe, Vl.G. Tyuterev, and A. Chichery, *High resolution IR spectra of the ozone molecule*, Atmos. Oceanic Opt. **12**, 771−785 (1999).

65. B.Y. Chang, C.Y. Kung, C. Kittrell, C.W. Hsiao, B.R. Johnson, S.G. Glogover, and J.L. Kinsey, *High-accuracy measurement of vibrational Raman bands of*

ozone at 266 *and* 270 nm *excitations*, J. Chem. Phys. **101**, 1914−1922 (1994).

66. R. Siebert, P. Fleurat-Lessard, R. Schinke, M. Bittererova, and S.C. Farantos, *The vibrational energies of ozone up to the dissociation threshold: dynamics calculations on an accurate potential energy surface*, J. Ch em. Phys. **116**, 9749−9767 (2002).

67. P. Rosmus, P. Palmieri, and R. Schinke, *The asymptotic region of the potential energy surface relevant for the* $O+O_2 -> O_3$ *reaction*, J. Chem. Phys. **117**, 4871−4877 (2002).

68. A. Barbe, VI.G. Tyuterev, S.A. Tashkun, M.-R. De Backer-Barilly, and M.T. Bourgeois, *New analysis of dense spectra of ozone isotopic species* $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{18}O$, $^{16}O^{18}O^{16}O$, *and* $^{18}O^{16}O^{18}O$ *assisted with global predictions*, in: *MODAS* Irkutsk, Russia (2001).

69. VI.G. Tyuterev, S.A. Tashkun, D.W. Schwenke, and A. Barbe, *An accurate isotopically invariant potential function of the ozone molecule near the open state equilibrium determined from spectroscopic data* (to be published).

70. A. Chichery, A. Barbe, VI.G. Tyuterev, and S.A. Tashkun, *High resolution IR spectra of* ^{18}O-*enriched ozone: band centers of* $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{18}O$, $^{18}O^{16}O^{18}O$, *and* $^{16}O^{18}O^{16}O$, J. Mol. Spectrosc. **205**, 347−349 (2001).

71. M.-R. De Backer-Barilly, A. Barbe, VI.G. Tyuterev, A. Chichery, and M.T. Bourgois, *High-resolution IR spectra of the* $^{16}O^{18}O^{16}O$ *in the range* 900−5000 cm^{-1}, J. Mol. Spectrosc. **216**, 454−464 (2002).

72. M.-R. De Backer-Barilly, A. Barbe, S. Tashkun, and VI.G. Tyuterev, *The* 5v_3 *bands of* ^{18}O *enriched ozone: line positions of* $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{18}O^{18}O$, *and* $^{18}O^{16}O^{18}O$, Molecular Physics **100**, 3499−3506 (2002).

73. A. Flaud, O. Vattinen, and A. Campargue, J. Mol. Spectrosc. **190**, 262 (1998).

74. O. Naumenko and A. Campargue, $H_2^{32}S$: *First observation of the* (70$^{±}$,0) *local mode pair and updated global effective vibrational Hamiltonian*, J. Mol. Spectrosc. **210**, 224−232 (2001).

75. J. Senekowitsch, S. Carter, A. Zilch, H.-J. Werner, N.C. Handy, and P. Rosmus, J. Chem. Phys. **90**, 783−794 (1989).

76. O.N. Sulakshina, Yu. Borkov, and VI.G. Tyuterev, *Calculating parameters of the* H_2S *molecule dipole moment function*, Atmos. Oceanic Opt. **14**, 753−761 (2001).

77. VI.G. Tyuterev, D.W. Schwenke, and S.A. Tashkun, *Intensities of isotopic species of hydrogen sulfide molecule from an accurate potential and dipole moment functions*, J. Chem. Phys., in preparation (2002).

78. VI.G. Tyuterev, S.A. Tashkun, D.W. Schwenke, L. Regalia, and Yu. Borkov, *Global calculations of IR transitions of 9 isotopic species* H_2S, D_2S, HDS *with substitutions* ^{32}S, ^{33}S, ^{34}S *and simulations of high-resolution spectra.* Work in progress (2003).