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Extension of the MIRS computer package for the modeling of molecular spectra : from effective to full *ab initio* ro-vibrational hamiltonians in irreducible tensor form

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Abstract

The MIRS software for the modeling of ro-vibrational spectra of polyatomic molecules was considerably extended and improved. The original version (Nikitin, et al. JQSRT, 2003, pp. 239–249) was especially designed for separate or simultaneous treatments of complex band systems of polyatomic molecules. It was set up in the frame of effective polyad models by using algorithms based on advanced group theory algebra to take full account of symmetry properties. It has been successfully used for predictions and data fitting (positions and intensities) of numerous spectra of symmetric and spherical top molecules within the vibration extrapolation scheme. The new version offers more advanced possibilities for spectra calculations and modeling by getting rid of several previous limitations particularly for the size of polyads and the number of tensors involved. It allows dealing with overlapping polyads and includes more efficient and faster algorithms for the calculation of coefficients related to molecular symmetry properties ($6C$, $9C$ and $12C$ symbols for C_{3v} , T_d , and O_h point groups) and for better convergence of least-square-fit iterations as well. The new version is not limited to polyad effective models. It also allows direct predictions using full *ab initio* ro-vibrational normal mode hamiltonians converted into the irreducible tensor form. Illustrative examples on CH_3D , CH_4 , CH_3Cl , CH_3F and PH_3 are reported reflecting the present status of data available. It is written in C++ for standard PC computer operating under Windows. The full package including on-line documentation and recent data are freely available at <http://www.iao.ru/mirs/mirs.htm> or <http://xeon.univ-reims.fr/Mirs/> or <http://icb.u-bourgogne.fr/OMR/SMA/SHTDS/MIRS.html>.

Key words: computational spectroscopy; *ab initio* calculations; vibration-rotation spectroscopy; effective hamiltonians; high-resolution infrared spectroscopy; polyads; irreducible tensors; molecular symmetry

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1 Introduction

Spectroscopic investigations of polyatomic molecules play a role of primordial importance for atmospheric applications. Effective hamiltonians in irreducible tensor operator (ITO) form have been successfully used to model the crucial effects of ro-vibrational perturbations on line positions and strengths through the analysis of complex interacting band systems (so-called polyads). An overview can be found in [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11] and references therein. This approach proved to be particularly efficient for a full account of the molecular and space symmetry properties. Hereafter we shall refer to these models as ITO spectroscopic models.

Nowadays, modern high-resolution and high-sensitivity techniques as well as direct spectroscopic observations of the planetary atmospheres and stars yield a wealth of spectroscopic data involving highly excited energy levels and relatively weak spectroscopic features. The modeling of such data using empirically adjusted effective hamiltonians becomes more and more complicated for several reasons. Most vibration-rotation bands show irregular perturbations due to accidental resonances. The importance of such effects in high-resolution spectroscopy has been shown in works by J.-M. Flaud, C. Camy-Peyret and co-workers [12, 13] who were among the first researchers developing effective model hamiltonians and dipole transition moment operators for asymmetric top molecules in case of resonance interactions. The number of interaction parameters grows very rapidly as the excitation increases. At high energy ranges which become experimentally accessible new inter-polyad resonances can occur requiring specific terms to be included in theoretical models. A. Barbe and co-workers [14, 15] have shown the crucial role of inter-polyad resonance perturbations and of perturbations due to «dark» (experimentally invisible) states, in particular for ozone spectroscopy in the range approaching the dissociation energy. The probability of near-coincidences of line frequencies rapidly increases with the number of atoms. For molecules of high-symmetry the combined effect of degeneracies and resonances makes it necessary to model a large number of strongly interacting bands simultaneously [1, 10, 11]. The choice of initial values for interaction parameters becomes arduous and the minimization process often reaches a local rather than global minimum. Another reason is a large proportion of dark states in complex and highly excited band systems and the corresponding deficit of experimental information. To some extent, accounting for unobserved energy levels is equivalent to introducing additional poorly defined parameters in effective models. On the other hand, full nuclear hamiltonians expressed in terms of normal-mode irreducible tensor operators can be obtained from *ab initio* potential energy surfaces (PES) as reported by Rey et al. [16, 17]. Then, non-empirical effective hamiltonians can be obtained using high-order contact transformations [18, 19, 20, 21] from a full nuclear hamiltonian. A large proportion of non-diagonal resonance parameters as well as diagonal parameters for dark states can be fixed to theoretical values derived from such transformations. Even though *ab initio* derived values for non diagonal parameters are approximate, they can describe the resonance couplings in a qualitatively correct way.

Ab initio vibration-rotation hamiltonians can be converted into irreducible tensor expansion [16, 17] which is formally similar to that employed for empirical effective hamiltonians [1, 22, 23] but interestingly they can be constructed up to higher order than in pure empirical approaches and are especially suitable for very highly excited band systems. Of course, the handling of ITO hamiltonian expansions built from PES relies on advanced computational efficiency. The performance of programming is important because of the very large number of hamiltonian terms and basis functions to deal with. For the validation of calculations it is necessary to check the convergence of contact transformations

[18, 19, 21] by achieving variational calculations with full nuclear hamiltonians. Such calculations are very cumbersome and require appropriate computational optimization. The development of efficient computational tools was crucial for the automatic generation and handling of various types of symmetry allowed terms simplifying in turn spectral analyses and spectroscopic data reductions.

The reader is referred to the original MIRS description [4] and to previous review articles for details on the effective hamiltonian tensorial approach and results [1, 22, 6]. The present paper is focused on the new computational features, illustrated by the results obtained so far.

2 Modeling principles

2.1 Irreducible tensor method

The irreducible tensor formalism and its computer implementation in MIRS code was already described in details in [22, 4] and references therein. Let us just remind that within the ITO formalism each elementary vibration-rotation term

$$h_{vib-rot} = t_{n_1 n_2 \dots m_1 m_2 \dots}^{\Omega_r(K.kC)} \mathbf{T}_{n_1 n_2 \dots m_1 m_2 \dots}^{\Omega_r(K.kC)} = t_{n_1 n_2 \dots m_1 m_2 \dots}^{\Omega_r(K.kC)} \beta (\epsilon \mathbf{V}_{n_1 n_2 \dots m_1 m_2 \dots} \otimes \mathbf{R}^{\Omega_r(K.kC)})_{A_1} \quad (1)$$

involved in the hamiltonian expansion is identified by rotational, vibrational and symmetry indices [24] according to the general nomenclature, where \mathbf{V} , \mathbf{R} and \mathbf{T} designate a vibrational, rotational and vibration-rotation tensor operators and t the corresponding parameters. Vibrational operators $\epsilon \mathbf{V}_{n_1 n_2 \dots m_1 m_2 \dots}$ are constructed in tensor form by recursive coupling of creation and annihilation operators associated to the normal modes of the molecule. The lower indices n_i and m_i being, respectively, the powers of creation and annihilation vibrational operators. The upper indices indicate the rotational characteristics of the considered term: Ω_r is the rotational power with respect to the angular momentum components; K is the tensor rank in the full rotation group; C is the rotational symmetry coinciding with the vibrational symmetry to satisfy the invariance condition under the molecular point group operations; β is a normalization constant introduced historically [24] to ensure the coincidence between some of the lower order standard and tensorial spectroscopic constants. Other notations follow references [1, 22, 4].

In MIRS, a specific coupling scheme [22] associated to a binary tree is applied directly to an arbitrary number of interacting vibrational modes and to arbitrarily high polyads. The construction of vibrational basis functions is achieved consistently from the action of creation operators on the vacuum function. This method is not only satisfying conceptually but also quite efficient for the computer calculation of matrix elements and commutators. The ro-vibrational terms are easily generated by further tensor couplings. The standard Amat and Nielsen classification scheme [25] is used in which the order of terms of the type H_{mn} is $m + n - 2$. Effective dipole moment (or other molecular property) expansions are represented in a similar manner as that of the hamiltonian but the full symmetry type has to be appropriately specified according to the molecular symmetry group [1, 22, 23]. For transformed dipole transition moments, terms of the type μ_{mn} are of order $m + n - 1$.

2.2 Inter-polyad couplings. Effective and full ro-vibrational hamiltonians

The effective model definition and associated quantum numbers are described in detail in Section 2.2 of ref. [4]. Only the basic features are summarized here in order to make the description of the new

implementation understandable.

The polyad structure constitutes the key for defining effective hamiltonians. For a given molecule, it is essentially governed by the number of the vibrational modes and their fundamental frequencies. In the most straightforward way the polyad scheme is build for vibrational *normal modes* coupled by vibration-rotation resonance interactions. As a preliminary step a reference energy level pattern is determined by resonance conditions defined by the user or by harmonic oscillator energies computed from the fundamental frequencies. Of course, the strength of a resonance perturbation depends not only on the proximity of the zero order energy levels but also on the coupling matrix elements. The MIRS code allows a certain flexibility for the polyad composition by optionally including or excluding some vibrational states according to estimations of coupling matrix elements. It is possible to take into account such physical considerations by playing with the resonance conditions. For instance, a gap between reference levels can be artificially increased in the case of weak vibration-rotation interactions or decreased in the case of strongly coupled but distant vibrational states. The true band centers remain unchanged under this operation. According to this approach the polyad structure of the molecule determines an effective hamiltonian expansion automatically implemented through the formal polyad expansion (see [1] for details)

$$H^{polyads} = H_{P_0} + H_{P_1} + H_{P_2} + \dots . \quad (2)$$

Vibrational matrix elements of the hamiltonian are computed in the harmonic oscillator zero-order approximation. The computation of rotational matrix elements is described in [26, 27, 28]. The irreducible tensor form [23, 1, 22, 6] implemented in the code allows a full account of symmetry properties. The polyad structure also determines the construction of the effective transition moments. It determines as well the quantum numbers used to label levels and transitions. Strict quantum numbers are related to the usual invariants : the polyad number P , the rotational quantum number J and the ro-vibrational symmetry species C .

It is well known that at a low energy range the polyad structure based on fundamental frequencies usually results in a good approximation for effective hamiltonians of semi-rigid molecules. For higher quantum numbers the modeling of experimental data can be considerably improved by including inter-polyad interactions. In the new version, all features concerning intra-polyad terms are conserved but inter-polyad terms can be added. More precisely any inter-polyad operator with rotational tensor powers equal to zero, one or two may be accounted for. This new feature may formally be expressed as

$$H = H^{polyads} + H^{inter-polyads} \quad (3)$$

$$H^{inter-polyads} = \sum H_{P_i/P_j} . \quad (4)$$

In this case, the polyad number P is no longer a strict quantum number. Approximate quantum numbers are generated using the eigenvector analysis. These approximate quantum numbers should correspond to quantum numbers of the zero-order harmonic-oscillator + rigid-rotor approximation under the condition that the corresponding physical quantities are kept near-invariant under the effect of perturbations.

In addition to effective ITO spectroscopic models, the new MIRS version offers a possibility of

Table 1: Data available from the MIRS package

Molecules	Spectral region	References
CH ₃ D	1500-3700	[8]
CH ₄	1700-4600	[11]
³⁵ CH ₃ Cl	0-2600	[7]
³⁷ CH ₃ Cl	0-2600	[7]
PH ₃	700-3500	[30]
CH ₃ F	Global	

variational computation of energy levels and wave functions from a full hamiltonian of nuclear motion in the ITO representation using symmetrized harmonic oscillator / rigid rotor basis set for a singlet electronic state. The tools of the MIRS code allow the generation of all necessary ITO terms up to a requested order of the expansions (1-4). All necessary matrix elements are calculated analytically without loss of precision. The values of t -parameters involved in these expansions have to be provided by the user as the input file for the program. These values can be computed from a given molecular *ab initio* or empirical PES according to the algorithm described in our recent works [16, 17] up to arbitrary orders. At a given order of expansion a full $H_{vib-rot}$ contains all non-zero symmetry allowed inter-polyad blocks in Eq.(4) systematically generated from an *ab initio* PES [16, 17]. Consequently this procedure usually accounts for many more vibrational interactions and the full hamiltonian contains more elementary ITO terms than an effective polyad model. Formally this corresponds to a summation over all inter-polyad couplings in Eq.(4). But contrary to an effective spectroscopic model all terms with rotational powers $\Omega_r > 2$ in the full hamiltonian expansion vanish by definition [29].

3 Updated database

The new version of the MIRS program contains a larger number of examples than the original version [4]. The package includes tutorial examples as well as complete projects related to recent analyses. New bands were added for CH₃D, ³⁵CH₃Cl, ³⁷CH₃Cl molecules. For CH₄ and PH₃ demonstrative examples are replaced by numerically correct models. A demonstrative model is also included for CH₃F based on a full ro-vibrational hamiltonian (Table 1).

A quite simple example is the sixth-order model for the ground-state, dyad, pentad and octad of ¹²CH₄. In this case, the vibrational coupling scheme coincides exactly with the one used in the STDS program [31]. This means that the effective parameter sets are identical in MIRS and STDS providing a good validation of both programs. For the following polyads (from the tetradecad upwards), even though the models are equivalent and include the same number of parameters at a given order of approximation, the two parameter sets are not in one to one correspondence. A similar system is illustrated with the sixth order model for the ground-state, dyad, pentad and octad of PH₃ [30].

The model for the lower two polyads (triad and nonad) of CH₃D represents a complex band system of a symmetric top molecule [8]. The parameters of the MIRS model have been fitted to some 12589 line positions and to 2400 line intensities with an accuracy close to the experimental precision (about 0.001 cm⁻¹ for positions and 4% for intensities). Altogether a common set of 441 effective hamiltonian parameters has been used to describe 13 vibrational states (ground state, triad, nonad) corresponding to 39 bands (6 fundamental, 3 overtone, 3 combination, and 27 hot bands). The intensities of the 9

bands involved in the nonad-ground state system were modeled at the second order of approximation using 83 effective dipole transition moment parameters.

Finally, results of the global analysis of the lower polyads of $^{12}\text{CH}_3^{35}\text{Cl}$ and $^{12}\text{CH}_3^{37}\text{Cl}$ are included. A preliminary analysis of the infrared spectrum in the region from 0 to 2600 cm^{-1} was performed using 288(303) effective parameters for isotopomers $^{12}\text{CH}_3^{35}\text{Cl}(^{12}\text{CH}_3^{37}\text{Cl})$ to model five lower polyads (17 vibrational states) [7]. The precision on positions is of the order of 0.0007 cm^{-1} .

4 Applications

4.1 Basic applications

The basic applications already implemented in the original version [4] are maintained in the new one. Complete files of energy levels can be calculated using the command `Calculus > build`. Each record contains the energy value, the set of rigorous quantum numbers (total angular momentum J , symmetry point group irreducible representations and ranking number) as well as approximate quantum numbers derived from the coefficients of the eigenvector expansions in the initial basis set. Details on the experimental measurements fitted are also provided. The number and the root-mean-squares (rms) deviations of assigned transitions are given together with the corresponding averaged observed minus calculated residual for every example. The partition function can be derived from the calculated levels involved in the model or set to an appropriate external estimate [32]. Several output formats including those of HITRAN [33] and GEISA [34] can be selected. The temperature and intensity threshold can be adjusted to meet specific needs for applications.

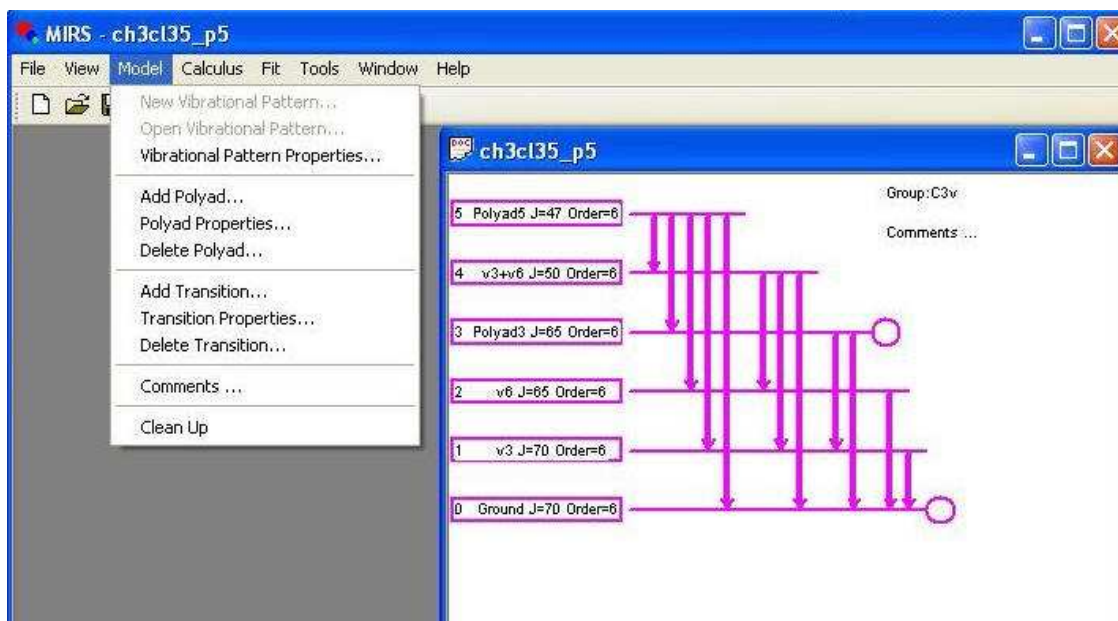
4.2 Advanced applications

4.2.1 Setting up new models

In order to set up a new model it is necessary to define the polyad structure and to introduce the modeling parameters. The modeling parameters are: (i) the symmetry point group of the molecule, (ii) the harmonic frequencies of the considered normal modes, (iii) the corresponding symmetry species (irreducible representations), (iv) a frequency gap used for gathering the subsequent vibrational sublevels into relevant vibrational polyads. Note that in the modeling procedure the frequencies can be entered in arbitrary units and do not need to match exactly the physical frequencies in order to provide flexibility. For example, the modeling of the CH_3D molecule was performed by setting the six fundamental frequencies to 2, 2, 1, 2, 1, 1 respectively and the frequency gap to 0.1. This yielded the triad and nonad structure described in [10, 8]. For CH_3Cl the situation was more complex and the fundamental frequencies were set closer to the actual values: 2968, 1354, 733, 3039, 1452 and 1018, respectively with a frequency gap of 200 (Fig. 1) [4, 7, 35]. This method of the model set up is quite general. For example choosing a large energy gap results automatically in including a maximum of symmetry allowed vibration-rotation interaction terms. Then by removing some of them (via text-editor) one can build a model suitable for describing observed resonance perturbations in molecular spectra. By this way one can easily build an «*overlapping-polyad*» model in order to account for inter-polyad resonances. In all cases, the resulting polyad structure can be displayed for checking and modifying purposes.

By default, MIRS is set to build effective hamiltonian matrices and transition moments according to the vibrational extrapolation scheme in the normal mode harmonic oscillator basis. This means

Figure 1: MIRS screen copy showing the model definition for CH₃Cl



This model includes the ground state and the lower five polyads of CH₃Cl. The arrows represent the band systems involved : 5 originating from the ground base, 3 from the ν_3 band, 2 from the ν_6 band, 1 from polyad 3 and one from the $\nu_3 + \nu_6$ band. The circles represent pure rotational transitions within the ground state and polyad 3 upper states. All the corresponding observed data (energy levels, line positions and line intensities) can be fitted coherently.

that for a given molecule a common set of effective hamiltonian parameters is set up to fit and predict the subsequent vibrational polyads. The same scheme applies for transition moment parameters. For instance a band system from the ground state to a given polyad and all the corresponding hot band systems are described by a common set of effective parameters. Such features are generated automatically by the program and controlled by a few basic modeling parameters entered through the window menu reproduced in Fig. 1.

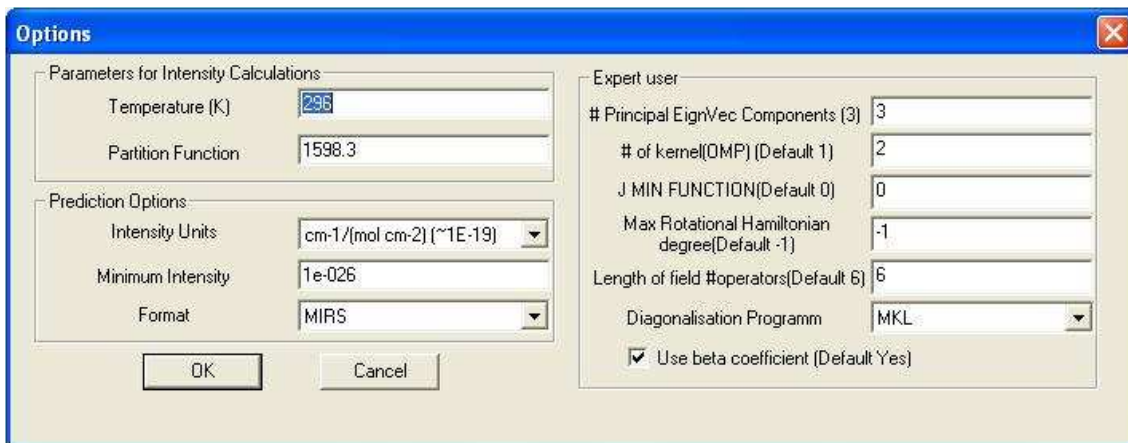
The nuclear spin statistical weights involved in intensity calculations are also manually introduced at this stage. Once the vibrational model is set up, the polyads and the transitions to consider are entered through another window menu exemplified in Fig. 2. For each polyad the order of the hamiltonian expansion and the maximum value of J has to be entered. Similarly, for each type of transitions the order of the effective dipole moment expansion has to be specified.

At the end of the procedure the build command generates all internal files needed for subsequent calculations. The same command is used to update all files whenever needed. The other commands of the Calculus menu displayed in Fig. 2 are generally self-explanatory. More details are available from the Help command. Thanks to its intrinsic flexibility MIRS can also be used to create quantum model hamiltonians not necessarily connected to real molecules. For instance, various systems involving coupled harmonic or anharmonic oscillators can be simulated numerically for further theoretical investigations.

4.2.2 Experimental data fitting (positions and intensities)

MIRS offers extensive set of tools for a non-linear least-squares fit of spectroscopic data (positions and intensities). According to the vibrational extrapolation scheme [1] well suited for global analyses,

Figure 2: MIRS option window



Refer to the Web site for explanations about non trivial options

the program is set to fit simultaneously all transitions and/or vibration-rotation levels involved in a given project. The fit of intensities is also achieved using a non-linear least-squares procedure with an adequate weighting already described in [31, 36]. Note that in our approach a rigorous consistency is de facto applied between intensity and position fits. The reader is referred to the original paper [4] for details on the sophisticated algorithms developed to overcome the increasing complexity of the problems to solve.

In the new version, two subprograms have been added to handle the adjustable parameters and their possible constraints. The Tools menu includes the Free_Parameters item to release all parameters that were previously fixed automatically by the program. The Copy_Parameters item allows the copy of parameters from one file to another. This is especially useful when one needs to change the model, for example to increase the order of the hamiltonian expansion.

Another improvement has been added to manage situations encountered when approximate quantum numbers are not physically meaningful and well conserved. The assignment of observed to calculated data is based on the rigorous quantum numbers. For an isolated polyad model these are: P (polyad number), J (total angular momentum), C (symmetry species) and the ranking index n within each P, J, C block. In some cases of nearby eigenvalues the ranking indices may undergo permutations from one iteration to another resulting to undesirable assignment jumps. MIRS allows temporarily removing from the fit the assigned levels which present such behavior by detecting anomalous variations of the scalar product of the corresponding eigenvectors during the iteration process. For this one needs to calculate at least parts of the eigenvector matrix α . If $f_i^{(0)}$ designates the i^{th} initial eigenfunction within a given P, J, C block and $f_j^{(k)}$ the j^{th} current eigenfunction within the same P, J, C block, the above mentioned scalar product can be expressed as

$$\langle f_j^{(0)} | f_i^{(k)} \rangle = \sum_{\sigma\delta} \alpha_{j\sigma}^{(0)} \alpha_{i\delta}^{(k)} \langle \sigma | \delta \rangle = A_{j,i}, \quad (5)$$

where σ and δ denote basis functions. For the great majority of the eigenvectors the scalar product (5) is close to unity and equivalently the A matrix is almost diagonal. In a minority of cases this is no longer true. For example an A matrix of the form

$$A = \begin{bmatrix} \dots & \dots & \dots & \dots & \dots & \dots \\ & 0.98 & 0.01 & 0.00 & 0.00 & \dots \\ & & 0.20 & 0.97 & 0.14 & \dots \\ & & & 0.20 & 0.14 & \dots \\ & & & & 0.65 & \dots \\ & & & & & \dots \end{bmatrix} \quad (6)$$

illustrates a situation where the two vectors corresponding to the middle of the matrix are rearranged while the first vector, associated to the diagonal element equal to 0.98, keeps its initial n index. Sometimes the rearrangement is not obvious, for instance when the diagonal element is not close to unity and simultaneously all non-diagonal values are not very large. This applies for the fourth vector of the matrix 6 with diagonal matrix element equal to 0.65. In this case the corresponding level must be excluded from the fit at least temporarily. The file with the initial eigenvectors is saved before the fit. For every iteration, some of the assigned levels are excluded from the fit and part of the levels previously excluded are re-assigned. If a large proportion of levels are excluded from the fit, then the iteration is unsuccessful and it becomes necessary to decrease the allowed variations for the parameters.

The fit of intensities is also subject to specific problems. Specific features to handle relative signs between transition parameters and interaction hamiltonian parameters are already described in section 4.3 of Ref. [4].

Despite all the above advanced options, it should be emphasized that in any case a purely automatic selection of adjustable terms for positions or intensities in an arbitrarily built model is not recommended. All procedures have to rely on physical considerations and depend on experimental data set and observed perturbations involved.

4.2.3 Group theory re-coupling coefficients and commutator-algebra calculations

The calculations involved in effective hamiltonians for highly excited states can be also very cumbersome and requires program optimization. It was found that one of the bottlenecks is the slow calculation of $9C$ [1] (other notations: X [37], 9Γ symbols[23]). The $12C$ symbols are required only for intensity calculations while $9C$ are used for line position calculations. In addition, $9C$ symbols are used in variational programs designed for the calculation of multidimensional irreducible matrix elements [38, 39, 40]. In the present version of MIRS, the calculation of $6C$, $9C$ and $12C$ symbols for C_{3v} , T_d , and O_h point groups is based on the improved algorithms reported in [41] which is much more efficient than in the program previously used. This new algorithm [41] uses the symmetry relations between even and odd representations. It allows one to speed up the C -symbol calculation and increase the efficiency of spectroscopic programs based on the irreducible tensorial formalism.

MIRS can also be used by expert users to generate various types of coupling coefficients as well as commutators of ITOs in algebraic or numerical formats. Such tools can be useful for the theoretical investigation of the fundamental properties of effective models and for establishing their relations with the full nuclear hamiltonian. It is well-known that, in general, an effective Hamiltonian is not uniquely determined from its eigenvalues [42, 43, 44, 45, 46, 47]. The ambiguity of the determination of H^{eff} from experimental energies is particularly important in the case of resonance interactions due to quasi-degeneracies of vibrational states [45, 48, 49, 50, 51]. In order to improve the convergence of least-square fits to experimental spectra and to obtain a unique set of fitted parameters, the spectroscopic effective

Table 2: Symbolic coding of vibrational powers

Numbers	Symbols
0, 1, 2, ..., 9	0, 1, 2, ..., 9
10, 11, 12, ..., 35	A, B, C, ..., Z
36, 37, 38, ..., 61	a, b, c, ..., z
62, 63	{,
> 63	?

hamiltonian models have to be constrained using the so called «reduction theory» [42, 52, 48, 53, 51, 54, 55]. The latter relies on extended commutator / anti-commutator algebra calculations. This Lie algebra of ITO plays a key role for a full account of symmetry properties in the contact transformation method [46, 23, 56].

4.2.4 Generation of symmetry allowed terms in the irreducible tensor form

We have added into the new MIRS a possibility for the user to generate a list of symmetry allowed terms involved in the ITO normal mode expansion of either an effective polyad hamiltonian (including inter-polyad interactions), or of an effective dipole moment or of the potential energy function up to an arbitrary order. For example, the list of ITO terms involved in a second order PES expansion for an XY_4 molecule can be obtain from the menu «tools > build parameters» by choosing «type of file = PES», then by choosing a vibrational pattern, and finally by defining the desired model. A similar MIRS tool is also operational for listing all allowed ITO terms involved in generators of unitary transformations which preserve group symmetry, time reversal and hermicity properties of transformed physical properties of a molecule. The present version of the package includes a sample example of symmetry allowed terms in S-generators involved in the problem of the effective hamiltonian reduction for the triad of CH_3D .

5 Modified specifications

5.1 Vibrational and Ro-vibrational calculation

All MIRS parameter files, dipole moment files and basis function files are text files. In order to calculate highly excited states using full nuclear hamiltonians a new coding of the symmetric powers (l, m, n) [22] was necessary. The original version of the program used only digits 0, ..., 9 for triplet numbers (l, m, n) . So only symmetric powers up to 9 were available although new applications required numbers with two digits. To ensure the compatibility with the original version and to preserve a good legibility for low symmetric powers, we decided to keep one single symbol according to Table 2. Note that now the number of polyads is limited to 99 which is far beyond the limit of realistic calculations.

5.2 Options

For efficient calculations on multi-processor (multiprocessors) computers, the new MIRS program uses OpenMP version 2.0 (<http://openmp.org>). Up to 8 kernels can be used simultaneously for matrix element calculations. As mentioned previously the full ro-vibrational hamiltonian contains terms up to the second rotational power only, while effective hamiltonian may contain all possible rotational

powers. Different programs may be used for eigenvalue calculation (see Diagonalization option). It is sometimes convenient to store on disk the full matrix for each P, J, C block because the diagonalization of a large number of matrices may be very burdensome.

5.3 Limitations

The previous version of the MIRS code was a 32-bit one with considerable restrictions on the number of tensors involved regarding the power of hamiltonian expansions and the size of polyads. The present version extends the number of polyads P from 9 to 99 while the number of terms and the polyad size is limited by the available computer memory. In order to speed-up calculations, sufficient computer resources are required to store all vibrational matrix elements in random access memory. The number of molecular vibration modes is limited to 20 and the maximum total angular momentum quantum number J for the T_d point group is limited to 199 [57].

6 Getting and installing

The MIRS package can be downloaded freely from our Web sites <http://www.iao.ru/mirs/mirs.htm>¹ and as supplementary data in the online version of the article. It consists of a self-extractive archive containing various tutorial examples. MIRS, written in C++, includes all necessary executable files for Windows XP and higher. Two versions (32 bit and 64 bit) of executable files are available. MIRS 64 bit works only on 64 bit windows operating systems. The major part of the examples based on effective hamiltonians (except CH4_polyad7 and CH4_polyad9) can be run using the 32 bit version. Fit operations can be run on the 32 bit version only. As a rule, full hamiltonian examples can be calculated using the 64 bit version only. Memory, CPU and disk space requirements depend on the complexity of the project. The package itself requires a minimum of 15 MB of free disk space. The tables of coupling coefficients occupy up to 150 MB when the highest J value considered so far (80) is involved. All examples and projects included in the package can be executed using a computer with at least 2 GB RAM and 500 MB of free disk space. A typical execution time using a processor at 2 GHz is about 10 min to build the CH₃D project (all matrix elements and prediction files) and less than 15 min to build each of the CH₃Cl projects. System requirements for complex examples are described in readme.txt files. For example CH4_polyad9 can be calculated only on computer with at least 24GB of memory and 160GB of free disk space. Standard features and options are directly accessible from the tutorial projects in which all necessary modeling files are included. The Help menu can be accessed at any stage of the project building and subsequent calculations. Refer to our Web sites for complete installation and running instructions.

7 Conclusion

The rapid increase of computer power and the progresses in multiprocessor parallelization have opened the way to considerable improvements of theoretical predictions and data reduction for complex high-energy band systems of polyatomic molecules. This may help in understanding new spectra involving high vibration-rotation excitations which have become experimentally accessible recently or can be available in future. Efficient modeling of spectra requires the development of advanced

¹also available from <http://xeon.univ-reims.fr/Mirs/> or <http://icb.u-bourgogne.fr/OMR/SMA/SHTDS/MIRS.html>

software specifically optimized for these purposes. Various methods and program implementations have been developed for computation of molecular spectra either from effective spectroscopic models [58, 55, 31, 1, 12, 59, 60, 61] (and references therein) or from potential and dipole moment surfaces using variational approaches [62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72], discrete variable representation (DVR) [73, 74, 75, 76, 77, 78] or filter-digitalization [79] techniques. A comparative analysis of advantages and limitations of these approaches is beyond the scope of the present paper (see ref. [80] for some related discussion). Complementary results for non-empirical effective hamiltonians and molecular spectra can be obtained via perturbation theory and Contact Transformation methods [81, 25, 52, 45, 46, 82, 13, 83, 55, 18, 20, 21]. An efficient computational software for the experimental data reduction in molecular spectroscopy and for the generation of line list parameters allows completing and extending spectroscopic databases which are planned to be linked in frame of the «Virtual Atomic and Molecular Data Center» (VAMDC) European project [84].

The reported extension of the MIRS computer package is designed to fully account for symmetry properties by using irreducible tensor representations for all physical properties and operators involved in direct calculations as well as in experimental molecular spectra fitting. Its particular feature is a unified treatment of effective polyad models (with the possibility of including explicitly inter-polyad interactions) and of full ab initio hamiltonian normal mode expansions in the frame of the ITO formalism. The new MIRS includes more efficient and faster algorithms for the calculation of coefficients related to molecular symmetry properties ($6C$, $9C$ and $12C$ symbols for C_{3v} , T_d , and O_h point groups) and for a better convergence of least-square-fit iterations. Several user-friendly tools are included dealing with the ITO algebra and with the generation of symmetry allowed terms in spectroscopic effective hamiltonians, transition moment operators, potential energy function, full ab initio hamiltonian expansions, and unitary transformations involved in the data reduction theory. This approach combined with an appropriate implementation of the high-order Contact Transformation method [18, 19] can be used, in principle, to perform a systematic computation of ab initio values of resonance coupling parameters in spectroscopic hamiltonians which were poorly determined in purely empirical models. The derivation of spectroscopic models for the CH_3Cl , CH_3Br , CH_3I , GeH_4 , AsH_3 molecules constructed in this way is currently in progress. We plan to provide in future a UNIX/LINUX version of MIRS.

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Installation package

The installation package is freely available from the attached file.

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