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Heuristic computation of the rovibrational \mathbf{G} matrix in optimized molecule-fixed axes. Gmat 2.1 [☆]

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ARTICLE INFO

Article history:

Received 19 February 2010

Received in revised form 19 April 2010

Accepted 23 April 2010

Available online xxxx

Keywords:

Rovibrational \mathbf{G} matrix

Rotation matrix

Optimal Euler angles

Unambiguous molecule-fixed axes

ABSTRACT

Gmat 2.1 is a program able to compute the rovibrational \mathbf{G} matrix in different molecule-fixed axes extending the capabilities of Gmat 1.0. The present version is able to select optimal molecule-fixed axes minimizing the pure rotational kinetic elements, the rovibrational kinetic elements or both simultaneously. To such an end, it uses a hybrid minimization approach. Thus, it combines a global search heuristic based in simulated annealing with a gradient-free local minimization. As the previous version, the program handles the structural results of potential energy hypersurface mappings computed in computer clusters or computational Grid environments. However, since now more general molecule-fixed axes can be defined, a procedure is implemented to ensure the same minimum of the cost function is used in all the molecular structures. In addition, an algorithm for the unambiguous definition of the molecule-fixed axes orientation is used.

Program summary

Program title: Gmat 2.1

Catalogue identifier: AECZ_v2_0

Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AECZ_v2_0.html

Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland

Licensing provisions: Standard CPC licence, <http://cpc.cs.qub.ac.uk/licence/licence.html>

No. of lines in distributed program, including test data, etc.: 52 555

No. of bytes in distributed program, including test data, etc.: 932 366

Distribution format: tar.gz

Programming language: Standard ANSI C++

Computer: All

Operating system: Linux, Windows

Classification: 16.2

Catalogue identifier of previous version: AECZ_v1_0

Journal reference of previous version: Comput. Phys. Comm. 180 (2009) 1183

Does the new version supersede the previous version?: Yes

Nature of problem: When building molecular rovibrational Hamiltonians, the kinetic terms depend on the molecule-fixed axes orientation. Thus, an appropriate orientation can significantly simplify the treatment of pure rotation and rovibrational coupling. The kinetic terms are collected in the rovibrational \mathbf{G} matrix. Thus, selection of an appropriate molecule-fixed reference frame is equivalent to localize the axes that minimize specific \mathbf{G} matrix elements. From this standpoint, three different kinds of molecule-fixed axes are of interest: first, axes minimizing pure rotational elements of the \mathbf{G} matrix; second, axes minimizing all the rovibrational \mathbf{G} matrix elements; third, axes minimizing simultaneously pure rotational + rovibrational coupling elements.

Solution method: In order to carry out the optimal selection of molecule-fixed axes, we add a hybrid method of minimization to the capabilities included in the first version of the program [1]. Thus, we minimize specific elements of the rovibrational \mathbf{G} matrix. To such an end, we apply a heuristic global optimization strategy, simulated annealing [2], followed by a Powell's local minimization [3]. We also

[☆] This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

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include a procedure to ensure that the same minimum is used when several molecular configurations are considered. In addition, an unambiguous molecule-fixed axes ordering is implemented.

Reasons for new version: The previous version of the program, Gmat 1.0, works in principal axes of inertia. Although this axes system is adequate for pure vibrational Hamiltonians, it is not always optimal for the construction of general rovibrational Hamiltonians. However, implementing the methods presented here, we can obtain molecule-fixed axes minimizing pure rotational or/and rovibrational interactions in the \mathbf{G} matrix. In this form, we can derive the simplest analytical form of the rovibrational Hamiltonian.

Summary of revisions: Some new methods have been introduced:

1. A method to build the molecule-fixed axes rotation matrix from the Euler angles.
2. Methods for rotating nuclear coordinates and their derivatives using the rotation matrix.
3. A method for applying simulated annealing to the search of the global minimum of a cost function formed by rotational or rovibrational \mathbf{G} matrix elements.
4. A method implementing Powell.

Running time: The sample tests take a few seconds to execute.

References:

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1. Introduction

A key point in the construction of rotation–vibration, rovibrational, molecular Hamiltonians is the rotating axes definition, *i.e.*, the selection of the molecule-fixed axes. An adequate selection of the molecule-fixed axes is the way to obtain the most simplified form of the Hamiltonian. This simplification appears in the kinetic part of the Hamiltonian, which is given by the elements of the rovibrational \mathbf{G} matrix [4,5].

With respect to the computation of the \mathbf{G} matrix, we have developed a software tool, Gmat 1.0, able to compute the \mathbf{G} matrix, in an arbitrary molecule, using principal axes of inertia as molecule-fixed system [1]. Whereas this is not a concern for pure vibrational Hamiltonians, this axes system is not necessary optimal for the construction of general rovibrational Hamiltonians. To such an end, we have recently proposed a new approach to the selection of optimal molecule-fixed axes [6]. This is based in the specific minimization of the pure rotational or/and rovibrational kinetic terms of the \mathbf{G} matrix.

Here, we present a new software tool, Gmat 2.1, which applies this approach using a hybrid simulated annealing + Powell's minimization algorithm. Thus, Gmat 2.1 is able to select optimal molecule-fixed axes minimizing pure rotational terms, rovibrational terms or both sets of terms simultaneously. In addition, Gmat 2.1 implements an algorithm for unambiguously defining the molecule-fixed axes orientation. Also, it ensures that the same minimum basin is used when different structures of the same molecule are considered. This is necessary to correctly compute the variation of the \mathbf{G} matrix as a function of the vibrational coordinates.

2. Theory

The ultimate goal is to build a rovibrational molecular Hamiltonian for a molecule with N nuclei. Considering generalized vibrational coordinates, q , the Hamiltonian takes the form [4,7],

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2} \sum_{i=1}^{3N-3} \sum_{j=1}^{3N-3} \left[g_{ij} \frac{\partial^2}{\partial q_i \partial q_j} + \left(\frac{\partial g_{ij}}{\partial q_i} \right) \frac{\partial}{\partial q_j} \right] + V(q_1, \dots, q_{3N-6}) \quad (1)$$

Our aim is to use a molecule-fixed axes system that simplifies Eq. (1). Since the potential, V , is invariant on the selection of reference axes, we focus in the kinetic term. The kinetic term of the

Hamiltonian, see Eq. (1), depends on g_{ij} , which are the elements of the rovibrational \mathbf{G} matrix [4,5]:

$$\mathbf{G} = \begin{pmatrix} \mathbf{G}_R & \mathbf{G}_{RV} \\ \mathbf{G}_{RV}^T & \mathbf{G}_V \end{pmatrix} = \begin{pmatrix} \mathbf{I} & \mathbf{X} \\ \mathbf{X}^T & \mathbf{Y} \end{pmatrix}^{-1} \quad (2)$$

In Eq. (2), \mathbf{G}_R and \mathbf{G}_V and \mathbf{G}_{RV} are the pure rotational, the pure vibrational and the rovibrational coupling submatrices. As shown in Eq. (2), \mathbf{G} is obtained in terms of the inertial tensor, \mathbf{I} , the pure vibrational \mathbf{Y} matrix, and the \mathbf{X} rovibrational interaction matrix. These matrices are obtained from the molecular structure [4]. The rotation from space-fixed to molecule-fixed axes is described by the rotation matrix, \mathbf{A} . Using the Euler angles, θ , ϕ , and ψ , \mathbf{A} is obtained as [8]:

$$\mathbf{A} = \begin{pmatrix} \cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & \cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi & \sin \psi \sin \theta \\ -\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & -\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi & \cos \psi \sin \theta \\ \sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta \end{pmatrix} \quad (3)$$

With the previous considerations, our problem is equivalent to select the molecule-fixed axes orientation that minimizes specific elements of the \mathbf{G} matrix. Since this orientation is given by the Euler angles (θ , ϕ , and ψ) the problem is equivalent to localize the global minimum of a cost function depending on these three parameters. This cost function is nothing but an appropriate selection of \mathbf{G} matrix elements. In the program, three cost functions are defined:

$$f(\mathbf{G}_R) = \sum_{i=1}^3 \sum_{j=i+1}^3 |g_{ij}(\theta, \phi, \psi)| \quad (4a)$$

$$f(\mathbf{G}_{RV}) = \sum_{i=1}^3 \sum_{j=3+i}^{3N-3} |g_{ij}(\theta, \phi, \psi)| \quad (4b)$$

$$f(\mathbf{G}_R + \mathbf{G}_{RV}) = \sum_{i=1}^3 \sum_{j=i+1}^3 |g_{ij}(\theta, \phi, \psi)| + \sum_{i=1}^3 \sum_{j=3+i}^{3N-3} |g_{ij}(\theta, \phi, \psi)| \quad (4c)$$

Case (4a) corresponds to minimizing the pure rotational non-diagonal terms of the 3×3 \mathbf{G}_R submatrix. Case (4b) minimizes

```

1  begin
2  switch (axes_type)
3  case principal axes of inertia:
4  diagonalize inertia tensor getting  $\theta, \phi, \psi$ 
5  end_case
6  otherwise:
7  if ( $\theta, \phi, \psi$  not fixed) then
8  if (global minimum desired) then
9  perform Simulated Annealing getting  $\theta, \phi, \psi$ 
10 end_if
11 perform local Powell's optimization getting  $\theta, \phi, \psi$ 
12 end_if
13 end_otherwise
14 end_switch
15 build rotation matrix,  $A$ , from  $\theta, \phi, \psi$ 
16 end

```

Fig. 1. High abstraction level pseudocode for the algorithm used to compute the different molecule-fixed axes in Gmat 2.1.

the rovibrational interaction submatrix \mathbf{G}_{RV} . Finally, case (4c) combines (4a) and (4b). With the optimal Euler angles found, we can build the corresponding \mathbf{A} rotation matrix, see Eq. (3). The molecular coordinates, \mathbf{r}' , and the rotated \mathbf{G}'_R and \mathbf{G}'_{RV} submatrices (\mathbf{G}_V is invariant) are obtained as:

$$\begin{aligned}
 \mathbf{r}' &= \mathbf{A} \cdot \mathbf{r} \\
 \mathbf{G}'_R &= \mathbf{A} \cdot \mathbf{G}_R \cdot \mathbf{A}^T \\
 \mathbf{G}'_{RV} &= \mathbf{A} \cdot \mathbf{G}_{RV}
 \end{aligned} \quad (5)$$

The program performs the global minimization using a hybrid simulated annealing + Powell's multidimensional direction set method. A detailed calibration of the procedure is given in [6]. In the present implementation, the program computes a total of four different molecule-fixed axes: principal axes of inertia, and the axes corresponding to the three cases in Eq. (4).

For a single geometry we have a single molecule-fixed axes system. However, when we consider the variation of \mathbf{G} along some vibrational coordinates, we have several molecular structures to process. In order the results to be comparable we need:

- To be always in the same basin of the cost function (which, beforehand, is not guaranteed to be the global minimum in all structures).
- To use always the same orientation of the optimal molecule-fixed axes.

These two conditions are satisfied in the program by using the algorithms described in the next sections.

2.1. Ensuring the use of the same minimum basin

Fig. 1 shows the high abstraction level pseudocode for the algorithm implemented to ensure the use of the same minimum basin when several molecular structures are used. Thus, when principal axes of inertia are requested, the rotation matrix, \mathbf{A} , is directly obtained by diagonalizing the inertia tensor. This is the only available option in the previous version of the program [1]. In the present version, two additional possibilities are available. The first one is to use always the optimal Euler angles found for a reference structure. The second is to start from the optimal Euler angles of a reference structure, performing a local minimization.

```

67 begin
68 if ( $\theta, \phi, \psi$  not fixed) then
69 // Building  $T$  matrix in order to get  $g_{aa} < g_{bb} < g_{cc}$ 
70 for ( $i \leftarrow 0$  and  $i \leftarrow 1$ ) do
71 select index,  $j$ , of max ( $g_{ii}$  to  $g_{22}$ )
72 build  $T_{ij}$ 
73 obtain  $\mathbf{G}_R \leftarrow T_{ij} \cdot \mathbf{G}_R \cdot T_{ij}$ 
74 obtain  $\mathbf{G}_{RV} \leftarrow \mathbf{G}_{RV} \cdot T_{ij}$ 
75 obtain  $\mathbf{A} \leftarrow \mathbf{A} \cdot T_{ij}$ 
76 end_for
77 // Defining a right handed  $a, b, c$  axes system
78 for ( $i \leftarrow 0$  and  $i \leftarrow 1$ ) do
79 compute rotated coordinate  $i$  of atom  $i$ :  $p \leftarrow \mathbf{A} \cdot \mathbf{X}_i$ 
80 if ( $p < 0$ ) then
81 change sign of row  $i$  in  $\mathbf{A}$ 
82 end_if
83 end_for
84 compute  $\mathbf{A}_3 \leftarrow \mathbf{A}_0 \times \mathbf{A}_1$ 
85 end_if
86 end

```

Fig. 2. High abstraction level pseudocode for the algorithm used to unambiguously select the a, b and c molecule-fixed axes orientation in Gmat 2.1.

When the same Euler angles are used for all the molecular structures, the \mathbf{A} matrix is build from the θ, ϕ , and ψ values given in the input. However, when the Euler angles are not considered fixed, Fig. 1 shows that we have two options. First, we can perform a full global minimum location, using simulated annealing, or, second, stay in the basin of a previous localized minimum. The first option is used to deal with a single molecular structure. It is also used to define a reference structure for the subsequent study of the \mathbf{G} matrix variation as a function of some vibrational coordinates. The second option allows the analysis of the \mathbf{G} matrix variation as a function of the vibrational coordinates.

When we are analyzing the variation of \mathbf{G} along several vibrational coordinates we have several molecular structures. As in the case of the Eckart axes [9], we use as reference the molecular equilibrium structure. The optimal θ, ϕ , and ψ values computed for it are the starting point for the local Powell's minimization in the rest of structures. Since local minimization methods cannot overcome maxima, we assure to remain in the original minimum, even if it becomes a local rather than a global one. In other words, we will just reorient the molecule-fixed axes in the same minimum found for the equilibrium structure.

2.2. Unambiguously defining the orientation of the molecule-fixed axes

Once optimal Euler angles are obtained, we need a uniform ordering of the molecule-fixed axes. The algorithm implemented in Gmat 2.1 is described in the pseudocode of Fig. 2. The first step is to label the axes as a, b , and c , according to the value of the diagonal elements of the pure rotation submatrix. For such an end, we follow the convention used for the principal axes of inertia, $g_{aa} < g_{bb} < g_{cc}$ [6]. To get the molecule-fixed axes in that order, we may need to interchange rows in the \mathbf{A} rotation matrix, see Eq. (3). So, we use an interchange elementary matrix $\mathbf{T}_{i,j}$ [6] switching rows i and j . When several interchanges are needed, we apply repeatedly the appropriate $\mathbf{T}_{i,j}$ matrices obtaining the global \mathbf{T} matrix as $\mathbf{T} = \mathbf{T}_{k,l} \cdot \mathbf{T}_{i,j}$. As shown in Fig. 2, $\mathbf{T}_{i,j}$ permits to compute the corresponding $\mathbf{G}_R, \mathbf{G}_{RV}$, and \mathbf{A} matrices.

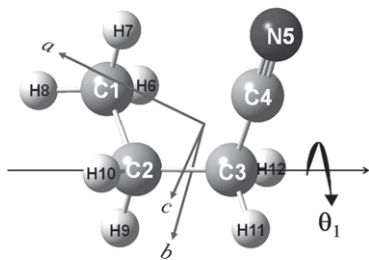


Fig. 3. Molecular structure and numbering convention of *n*-propyl cyanide. The nitrile torsion angle, θ_1 , is shown. The figure depicts the orientation of the molecule-fixed *a*, *b* and *c* axes for the *gauche* equilibrium structure.

The previous step selects *a*, *b* and *c* in the appropriate order, but it does not guaranteed the correct orientation of the axes. To such an end, we have developed the procedure shown in Fig. 2 for defining a **right-handed** *a*, *b* and *c* axes system. The procedure is more general and failproof that the one proposed originally in Ref. [6]. Fig. 2 shows that, first, we define the positive sense of the *a* and *b* axes such that the *a* and *b* coordinates of the first atom are positive. Since for the rotated coordinates we have $\mathbf{r}' = \mathbf{A} \cdot \mathbf{r}$, see Eq. (5), if the first or second coordinates of \mathbf{r}' are negative, we must invert the sign of the corresponding row in the \mathbf{A} matrix. Second, to obtain a **right-handed** frame, we consider that the first row of \mathbf{A} (\mathbf{A}_0) gives us the coordinates of a unit vector on the pos-

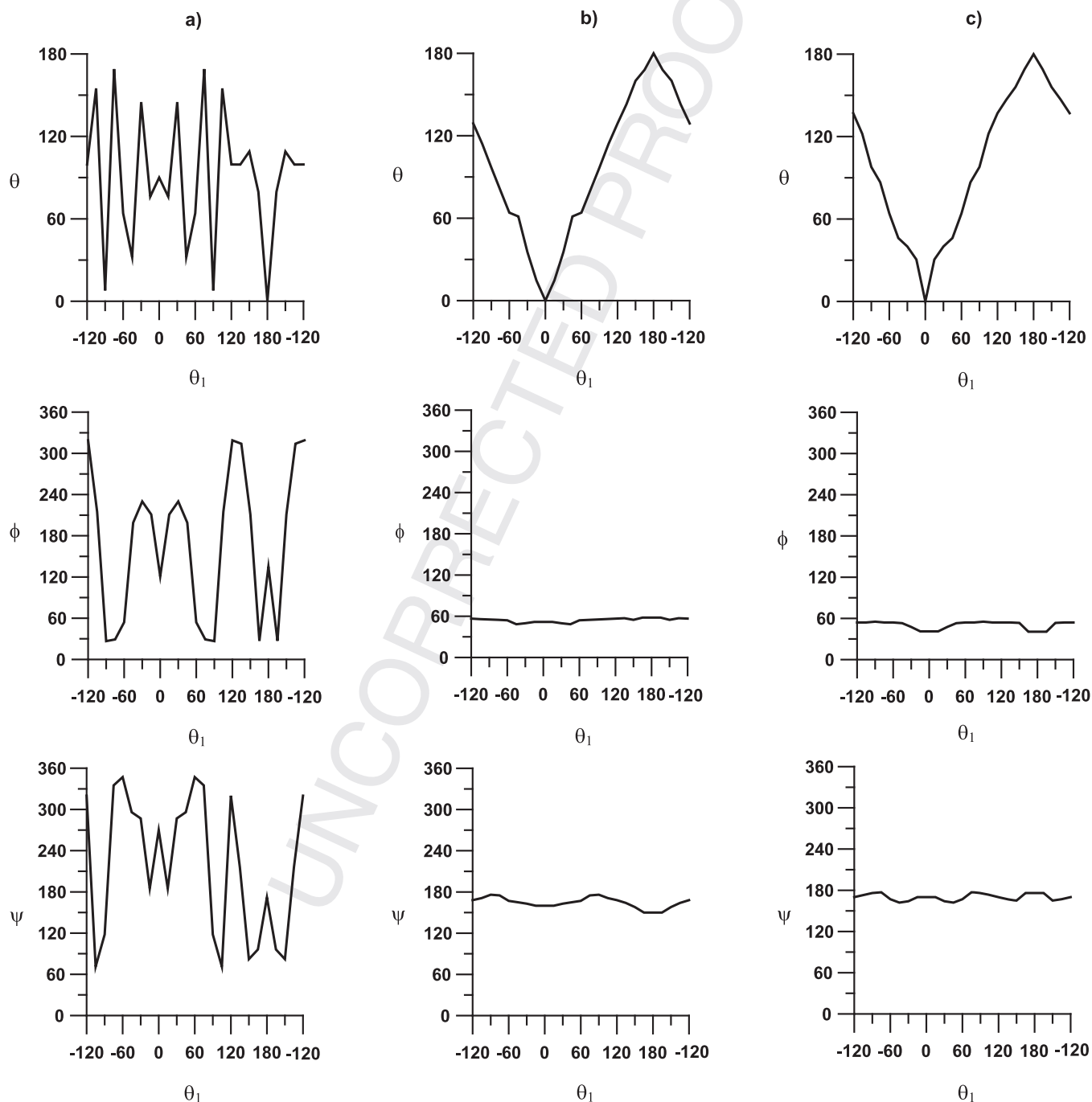


Fig. 4. Value of the optimal θ , ϕ , and ψ Euler angles as a function of the nitrile torsion angle, θ_1 , in *n*-propyl cyanide. Panel a), results obtained using global optimization for each molecular structure. Panel b), results obtained with the optimal Euler angles of the reference structure and the algorithm for unambiguously referring the molecule-fixed axes. Panel c), results obtained with local minimization in the reference structure basin and the algorithm for unambiguously referring the molecule-fixed axes.

itive a semiaxis. Analogously, the second row of \mathbf{A} (\mathbf{A}_1) gives a unit vector on the positive b semiaxis. Therefore, the positive c semiaxis, the third row of \mathbf{A} (\mathbf{A}_2), is obtained as the vectorial product of the first and second rows $\mathbf{A}_2 = \mathbf{A}_0 \times \mathbf{A}_1$. The whole procedure is equivalent to obtain the new rotation matrix as $\mathbf{B} \cdot \mathbf{A}$, where \mathbf{B} is defined as:

$$\mathbf{B} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \gamma \end{bmatrix} \quad (6)$$

with α , β , and γ equal to $+1$ or -1 depending on if it was necessary to invert or not the sense of the a , b , and c axes, respectively.

After applying the algorithms depicted in Figs. 1 and 2, we have unambiguous results for analyzing the variation of the rovibrational Hamiltonian kinetic terms as a function of the vibrational coordinates.

3. Application

The effect of the previous algorithms is exemplified using a molecule of astrophysical interest, the n -propyl cyanide [10]. This molecule exhibits two stable and spectroscopically distinguishable conformations: *gauche* and *trans* with respect to the methyl (CH_3) and nitrile (CH_2CN) moieties orientation. The *gauche* form is the most stable [10]. The n -propyl cyanide was identified in 2008 in star-forming regions in the interstellar medium, specifically in Sagittarius B2, Sgr B2(N) [11].

Here, we consider the variation of the n -propyl cyanide molecular structure as a function of the nitrile torsional angle. This angle is responsible for interconversion between the *gauche* and *trans* forms. Fig. 3 shows the molecular structure and the numbering convention used in this work. With this convention, the nitrile torsional angle, θ_1 , is defined as dihedral C4C3C2C1. We obtain the reference, equilibrium, structure of the molecule performing a full geometry optimization at the MP2/aug-cc-pVTZ theory level. Working at the same theory level, we obtain the molecular structures for θ_1 values ranging from 0° to 180° in increments of 15° . The molecule is symmetric with respect to the inversion of coordinates on the C1C2C3 plane. Thus, the range of θ_1 values considered expands the whole interval from 0° to 360° . All the calculations have been carried out with the Gaussian 03 suite of programs [12].

For the equilibrium structure, the θ_1 angle is found to be 61.1° . Considering this structure as the reference one, we use Gmat 2.1 to compute the molecule-fixed axes corresponding to case (4c). The resulting axes are shown in Fig. 3. We observe that the a - b plane is very close to the C1C2C3 molecular plane, which defines the original x and y space-fixed axes. In consequence, the c axis is approximately perpendicular to this plane, and near the z space-fixed axis.

To analyze the effect of the approaches implemented in the algorithms of Figs. 1 and 2, we compute the variation of the θ , ϕ , and ψ Euler angles as a function of the θ_1 torsional coordinate. As for the equilibrium structure, we consider case (4c). Fig. 4 collects the results.

Panel a) of Fig. 4 corresponds to the case when none of the present algorithms is applied. Here, an independent global minimum is located for each molecular structure. We observe that the evolution of the Euler angles is chaotic, due to the lack of a common reference system. Therefore, trying to express the \mathbf{G} matrix elements as a function of θ_1 for building the corresponding

rovibrational Hamiltonian is meaningless. The situation changes radically when we keep fixed the Euler angles obtained in the reference structure, and a common reference system is used applying the algorithm in Fig. 2. The results are shown in panel b) of Fig. 4. Here, we observe that the θ angle experiences a periodic variation with the nitrile torsion. On the other hand, ϕ and ψ remain almost constant. θ measures the angle between the molecule-fixed c and the space-fixed z axes. Thus, the results indicate that the effect of the nitrile torsion is an oscillation, back and forth, of the molecule-fixed axes with respect to the space-fixed z axis (the one perpendicular to the C1C2C3 plane). However, no significant rotation around the z axes seems to exist. Finally, panel c) in Fig. 4 shows the effect of including the local minimization, starting from the reference structure molecule-fixed Euler angles. We observe just minor differences with respect to the previous case. The overall trend is maintained.

The previous results show that the most important factor is the use of a reliable common reference for the molecule-fixed axes definition and orientation. On the other hand, we observe that to use directly the value of the Euler angles, from the equilibrium structure, or to look for a local minima from them provides similar results.

Acknowledgements

This work has been cofinanced by FEDER funds and the Consejería de Educación y Ciencia de la Junta de Comunidades de Castilla-La Mancha (grant # PBI08-0008). The Ministerio de Educación y Ciencia (grant # AYA 2008-00446) is also acknowledged.

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[2] [3]

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