COMPUTATION OF KINETIC CONSTANTS FOR LARGE RANGE INTERNAL MOTIONS IN MOLECULES

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Abstract—This paper presents the development of a software tool for the calculation of the rotational–vibrational G matrix. The program is applied to the study of the kinetic coupling between wagging and methyl torsion in acetone and acetaldehyde. An increase in the coupling is observed when the mass of the wagging atom or the mass of the molecule decreases. This fact becomes very important for the hydrogen wagging in the acetaldehyde molecule. The dependence of kinetic constants on the vibrational coordinates is also analysed. It is found to be small even in the case of large displacements from the equilibrium position.

INTRODUCTION

The usual treatment of molecular vibrations assumes a very small displacement of the atoms around equilibrium positions. Following this hypothesis, the Wilson's method of the F,G matrices uses a pure vibrational Hamiltonian where the potential function adopts a harmonic form and the kinetic part is separated from the overall rotation and expressed by constant terms (Wilson *et al.*, 1980).

However, there are several cases where the harmonic approximation is no longer valid. Thus, internal rotation, ring-puckering or inversion in molecules are examples of large range, non-harmonic motions, where the F,G treatment is not enough accurate. In such cases, the potential function can be expressed as a function of the large range coordinates (Lewis *et al.*, 1972; Harthcock & Laane, 1985; Smeyers *et al.*, 1990) and the kinetic part can be obtained through the rotational–vibrational G matrix rather than through the pure vibrational Wilson's G matrix (Pickett, 1972; Harthcock & Laane, 1985).

In this paper we present a program able to obtain the rotational–vibrational G matrix. The program has been developed for the treatment of large range vibrations. It is applied to the study of the kinetic coupling between methyl torsion and wagging (planar bending) motions in acetaldehyde and acetone (prototypes of molecules where internal rotations and wagging play an important role). The dependence of the kinetic terms on these vibrational coordinates is also considered.

THEORY

Given a molecule with n nuclei and two systems of coordinates, one fixed external to the molecule and the other internal, on the centre of mass, and with arbitrary axis orientation, the classical expression for the kinetic energy is (Wilson *et al.*, 1980)

$$T = \frac{1}{2} \sum_{\alpha=1}^{n} m_\alpha \mathbf{V}_\alpha \mathbf{V}_\alpha \qquad (1)$$

where

$$\mathbf{V}_\alpha = \mathbf{V} + (\omega \times \mathbf{r}_\alpha)Z + \sum_{i=6}^{3N} \frac{\partial \mathbf{r}_\alpha}{\partial q_i} \frac{\partial q_i}{\partial t} \qquad (2)$$

being $\mathbf{V}$ the velocity of the centre of mass, ω the angular velocity for the internal system, $\mathbf{r}_\alpha$ the position vector of the αth atom in the internal system, Z the director cosines matrix of the internal axis with respect to the fixed external ones and q_i any vibrational coordinates (we are not restricted to work with normal coordinates). It is interesting to note that the third term of equation (2) does not depend on the selected coordinates system. Neglecting the effect of translation, the equation (1) can be expressed in matrix notation as (Pickett, 1972)

$$2T = (\mathbf{P}^T, \mathbf{p}^T)\mathbf{G}\begin{pmatrix} \mathbf{P} \\ \mathbf{p} \end{pmatrix} \qquad (3)$$

where $\mathbf{P}$, the conjugate momenta with respect to the overall rotation, are given by

$$\mathbf{P} = (\partial T/\partial \omega) \qquad (4)$$

$\mathbf{p}$, the conjugate momenta with respect to the change on the vibrational coordinates, are given by

$$\mathbf{p} = (\partial T/\partial \mathbf{q}) \qquad (5)$$

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and **G** is the rotational–vibrational matrix, expressed as

$$G = \begin{pmatrix} I & X \\ X^T & Y \end{pmatrix}^{-1} \tag{6}$$

where **I** is the instantaneous inertial tensor representing the overall rotation contribution to the total kinetic energy, **Y** represents the pure vibrational part, which does not depend on the coordinates system, and **X** represents the rotation–vibration interaction. The components of these matrices are obtained as

$$I_{ii} = \sum_{\alpha}^{n} m_{\alpha}[(\mathbf{r}_{\alpha})^2 - (r_{\alpha i})^2] \tag{7}$$

$$I_{ij} = \sum_{\alpha}^{n} m_{\alpha} r_{\alpha i} r_{\alpha j} \tag{8}$$

$$X_{ij} = \sum_{\alpha}^{n} m_{\alpha} \left[\mathbf{r}_{\alpha} \times \left(\frac{\partial \mathbf{r}_{\alpha}}{\partial q_i} \right) \right]_j \tag{9}$$

$$Y_{ij} = \sum_{\alpha}^{n} m_{\alpha} \left(\frac{\partial \mathbf{r}_{\alpha}}{\partial q_i} \right) \cdot \left(\frac{\partial \mathbf{r}_{\alpha}}{\partial q_j} \right). \tag{10}$$

The study of pure vibrations considers only vibrational transitions between the ground rotational states (Lewis et al., 1972; Pickett, 1972; Harthcock & Laane, 1985). Thus, the kinetic operator, after transformation to the quantum-mechanical form (Podolsky, 1928), becomes

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=6}^{3N} \sum_{j=6}^{3N} \frac{\partial}{\partial q_i} \left(g_{ij} \frac{\partial}{\partial q_j} \right)$$
$$+ \frac{\hbar^2}{8} \sum_{i=6}^{3N} \sum_{j=6}^{3N} \left[\frac{\partial}{\partial q_i} g_{ij} \left(\frac{\partial \ln g}{\partial q_j} \right) - \left(\frac{\partial \ln g}{\partial q_i} \right) g_{ij} \frac{\partial}{\partial q_j} \right]$$
$$+ \frac{\hbar^2}{32} \sum_{i=6}^{3N} \sum_{j=6}^{3N} \left(\frac{\partial \ln g}{\partial q_i} \right) g_{ij} \left(\frac{\partial \ln g}{\partial q_j} \right) \tag{11}$$

where g represents the determinant of the G matrix. The second and third terms in equation (11) are regarded as a pseudopotential which is usually neglected or incorporated into the potential function. The magnitude of this pseudopotential is related to the change of the g determinant and the g_{ij} terms with the vibrational coordinates. This point will be considered further.

Neglecting the pseudopotential term, equation (11) becomes after rearrangement

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=6}^{3N} \sum_{j=6}^{3N} \left[g_{ij} \frac{\partial^2}{\partial q_i q_j} + \left(\frac{\partial g_{ij}}{\partial q_i} \right) \frac{\partial}{\partial q_j} \right]. \tag{12}$$

When the terms g_{ij} are considered constant only the first term in equation (12) remains.

The above expression is defined for the complete set of $3N - 6$ vibrations. However, the large range vibrations usually have low frequencies and, in a first approximation, they are separated from the rest of vibrations. Thus, equation (12) is typically used for the study of large range motions whereas the other vibrations are described by the Wilson's method.

PROGRAM DESCRIPTION

A software tool able to obtain the rotational–vibrational G matrix has been developed and implemented in standard FORTRAN 77 language (Muñoz-Caro & Niño, 1993). The program runs under the DOS and the UNIX operating systems. Molecular definition must be supplied through a Z matrix, being possible the treatment of deuterated species and the use of dummy atoms. A system of key words is used for the control of input data. The procedure developed for the reading of key words is shown in Fig. 1.

A logical model of the program from the standpoint of the functional behaviour, is shown in Fig. 2 as a data flow diagram (Martin & McClure, 1988; Yourdon, 1989). In this diagram arrows represent flows of data, squares represent terminal entities (the

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Begin procedure

Charact (80) is an array of characters
Keyword is a string of 5 characters
N and i are integer

For i=1 to 80
    Read Charact(i)
end_for

i←0
Repeat
    i←i+1

    if Charact(i) ≠ ' ' then
        Write in scratch file Charact(i) to Charact(i+4)
        Rewind scratch file
        Read keyword in scratch file
    end_if

    Repeat
        i←i+1
    until Charact(i) = '=' or i=80

    if i=80 exit procedure

    Repeat
        i←i+1
    until Charact(i) is a Number or i=80

    if i=80 exit procedure

    Write Charact(i) in scratch file
    Rewind scratch file
    Read N in scratch file

    Recognize Keyword and N

until i=80

End_procedure
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Fig. 1. Pseudocode for the reading key words procedure. The key words are used as follows: KEYWORD = N where N is an integer which defines the action symbolized by KEYWORD.
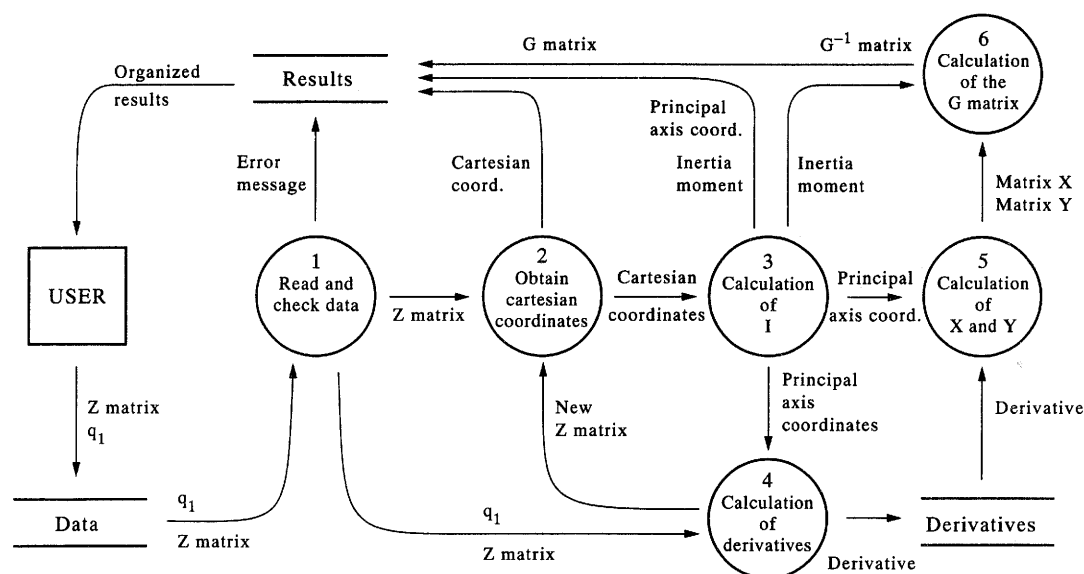
Fig. 2. Data flow diagram showing how the information is transformed and handled in the kinetic constants calculation program.

user), double lines represent files and bubbles represent processes transforming input data in output data. The functionality of the system has been partitioned in six processes, using an auxiliary file for storing the derivatives. Each process has been physically implemented in a separated file.

The program uses the principal axis system. The derivatives are calculated by finite differences and written in binary format to a direct access file. The matrix G^{-1} is inverted through a LU decomposition using standard algorithms (Press *et al.*, 1986). Finally, the vibrational terms, g_{ij}, are expressed in wavenumbers.

Calculation of derivatives

The derivatives of the nuclear positions with respect to the vibrational coordinates are calculated by central finite differences, i.e.

$$\frac{\partial \mathbf{r}_\alpha(q_i)}{\partial q_i} \simeq \frac{\mathbf{r}_\alpha(q_i + \Delta q_i) - \mathbf{r}_\alpha(q_i - \Delta q_i)}{2\Delta q_i} \tag{13}$$

being necessary to determine a value for Δq_i.

Two facts counteract in this kind of problems (Pople *et al.*, 1968). When Δq_i decreases, we obtain a better approximation to the derivative but the round off error increases. Thus, the increment, Δq_i, is calibrated for assessing the importance of both effects.
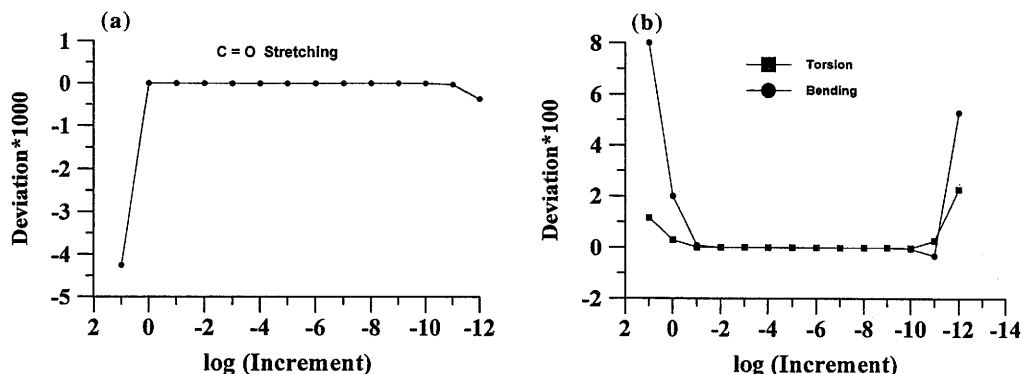

Fig. 3. Graphical representation of the calculated kinetic constants in the acetaldehyde molecule vs the increment of the internal coordinate used for the obtention of derivatives. Kinetic constants are expressed as deviation from the central values of 1.1116, 1.1313 and 7.8426 cm^{-1} for the C=O bond stretching, the C—C—O bending and the methyl torsion respectively. The internal coordinates increments are expressed as decimal logarithms. (a) C=O bond stretching. Increments in Å. (b) C—C—O bending and methyl torsion. Increments in deg.
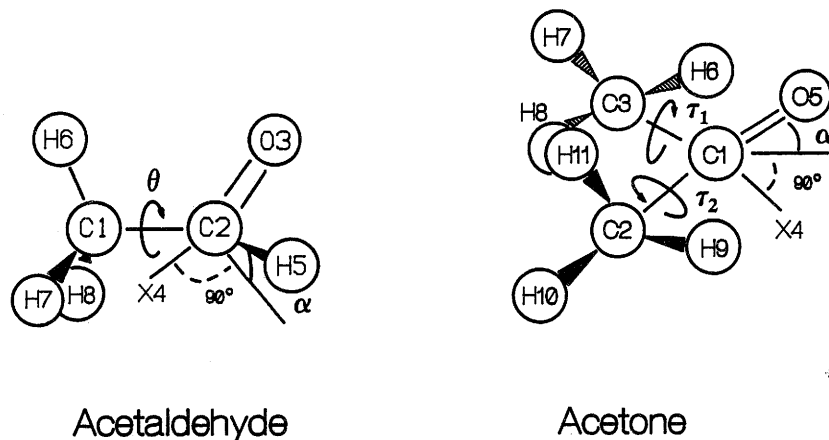
Acetaldehyde   **Acetone**

Fig. 4. Numbering convention and internal motions definition in the acetaldehyde and acetone molecules. The torsion motion in acetaldehyde is described through the $\theta(H_6$—C_1—C_2—$O_3)$ angle, whereas for acetone the angles $\tau_1(H_6$—C_3—C_1—$C_2)$ and $\tau_2(H_9$—C_2—C_1—$C_3)$ describe the two methyl rotations. The wagging angle is defined using the dummy atom X_4. The value of the valence angle between X_4, its bonded atom and the molecular plane is fixed to a value of 90 deg. Thus, the wagging motion is described by means of the dihedral angle $\alpha(H_5$—C_2—X_4—$C_1)$ in acetaldehyde and $\alpha(O_5$—C_1—X_4—$C_2)$ in acetone.

For calibration, the acetaldehyde molecule in the most stable conformation is used (Muñoz-Caro et al., 1994). The variation of the kinetic constants for the three kinds of internal coordinates is graphically shown in Fig. 3. Figure 3(a) shows the variation of the kinetic constant for the C=O bond stretching. It can be observed that the value of 1.1116 cm^{-1} remains unchanged in an interval ranging from 1 to 10^{-10} Å. Figure 3(b) represents the kinetic constant variation for the C—C—O bending and the methyl group torsion. In a similar way to the bond stretching case, the central values of 1.1313 and 7.8426 cm^{-1}, for bending and torsion are maintained constant for increments between 10^{-2} and 10^{-10} deg. Thus, values of 0.01 Å for bond lengths and 0.001 deg for valence and dihedral angles are selected as standard increments Δq_i.

Tests

The accuracy of the program has been tested by comparison with previously obtained results for internal rotation constants. Thus, the value of 7.84 cm^{-1} calculated in this paper for the methyl rotation constant of acetaldehyde can be compared to the value of 7.81 cm^{-1} (Ozkabak & Goodman, 1992) obtained through the reduced moment of inertia for internal rotation (Pitzer & Gwinn, 1942). In a similar fashion our values of 5.69 and -0.16 cm^{-1} for the methyl rotation and coupling constants in acetone compares well with the 5.69 and -0.17 cm^{-1} obtained through the reduced moment of inertia (Ozkabak et al., 1990).

APPLICATIONS

The kinetic coupling between rotation and wagging is investigated in some typical cases, acetaldehyde and acetone. Molecular kinetic constants are calculated for the most stable conformation (Muñoz-Caro et al., 1994; Ozkabak et al., 1990) in the ground state, see Fig. 4.

Tables 1 and 2 show the results for acetaldehyde and acetone respectively. In the case of acetaldehyde an important coupling $(g_{\alpha\theta})$ of -5.75 cm^{-1} is observed when both methyl torsion and hydrogen wagging are taking into account. The coupling is also observed in the increase of the g_α and g_θ terms from isolated $7.84/18.91$ cm^{-1} to simultaneous $9.32/22.46$ cm^{-1} motions. For acetone, Table 2 shows a small coupling constant, -0.17 cm^{-1}, between the two methyl torsions. This small coupling is also reflected in the unchanged value for $g_{\tau 1}$ (5.69 cm^{-1}) when the wagging is not considered. However, an increase in the methyl torsion and the methyl coupling constants is observed when the wagging is taking into account.

The coupling between torsions and wagging $(g_{\alpha\tau 1}, g_{\alpha\tau 2})$ is much smaller in acetone than in the case of acetaldehyde. Also, it is found a smaller value for the methyl torsion constant. These facts arise from two sources [equations (6)–(10)]. On one hand, the

Table 1. Kinetic constants (in cm^{-1}) for acetaldehyde

Constant	Torsion*	Wagging*	Torsion + wagging†
g_0	7.84	—	9.32
g_α	—	18.91	22.46
$g_{\alpha\theta}$	—	—	−5.75

* Isolated motion.
† Simultaneous motions.

Table 2. Kinetic constants (in cm^{-1}) for acetone

Constant	Torsion (τ_1)*	Torsions $(\tau_1 + \tau_2)$†	Torsions + wagging†
$g_{\tau 1}$	5.69	5.69	6.09
$g_{\tau 2}$	—	5.69	6.09
$g_{\tau 1\tau 2}$	—	−0.17	−0.56
g_α	—	—	1.80
$g_{\alpha\tau 1}$	—	—	0.85
$g_{\alpha\tau 2}$	—	—	−0.85

* Isolated motion.
† Simultaneous motions.

of the constants and the determinant have been obtained for several conformations using a grid size of 30 and 15 deg for the methyl torsion, θ, and the aldehydic wagging, α, angles respectively.

Figure 5 shows contour maps representing the variation of g_0, g_α and $g_{0\alpha}$ with the angles. The maps reflect a typical threefold symmetry arising from the methyl group structure. It is observed a decrease in the values of g_0 [Fig. 5(a)] and g_α [Fig. 5(b)] and an increase in $g_{0\alpha}$ [Fig. 5(c)] when going from $\alpha = 0$ deg to $\alpha = 45$ deg. The torsion constant, g_0, reaches a maximum of 9.36 cm^{-1} for $\alpha = 0$ deg, $\theta = 60$ deg. In the same conformation g_α adopts the maximum value, 22.49 cm^{-1} and $g_{0\alpha}$ the minimum, -5.80 cm^{-1}. The minimum for g_0, g_α and the maximum for $g_{0\alpha}$ appears for $\alpha = 45$ deg, $\theta = 0$ deg with values of 9.22, 20.89 and -5.13 cm^{-1} respectively. These results represent a relative variation of 1.49, 7.11 and 11.55% for the torsion, wagging and coupling respectively. However, the absolute magnitude of the changes is very small (the highest variation is found for torsion with a value of 1.60 cm^{-1}).

Figure 6 reflects the change in the natural logarithm of the g determinant as a function of the θ and α angles. The values range from a minimum of -10.5037 for $\theta = 30$ deg and $\alpha = 45$ deg to a maximum of -10.4717 for $\theta = 0$ or 60 deg and $\alpha = 0$ deg (planar conformations). The small change of 0.032 units in $\ln(g)$ supports the neglect of the pseudopotential term in equation (11).

CONCLUSIONS

A program for the calculation of the rotational–vibrational G matrix has been developed. It provides an useful tool for the study of large range movements.

The derivatives of the nuclear positions obtained through finite differences are fairly insensitive to the vibrational coordinates increment. Only for very small or very large increments a significant deviation from the average values can be observed. Thus, we
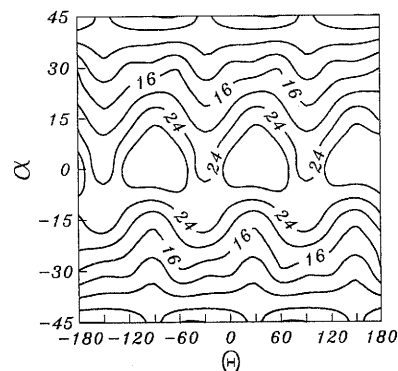
Fig. 5. Contour maps (in cm^{-1}) for the variation of the g_0, g_α and $g_{0\alpha}$ kinetic terms of acetaldehyde with the torsion, θ, and the wagging, α, angles. Variations are measured from the minimum values of $g_0 = 9.22$ cm^{-1}, $g_\alpha = 20.89$ cm^{-1} and $g_{0\alpha} = -5.80$ cm^{-1}. (a) Torsion constant, g_0. (b) Wagging constant, g_α. (c) Coupling constant, $g_{0\alpha}$.

higher mass of the wagging oxygen with respect to the wagging hydrogen. On the other, the higher mass of acetone with respect to the acetaldehyde molecule. Both effects contribute to decrease the kinetic constants values. Thus, the important value of the coupling in acetaldehyde is a consequence of the small mass of the hydrogen atom.

The change of kinetic constants and g determinant with the torsion and hydrogen wagging angles is investigated in the acetaldehyde molecule. The values

Fig. 6. Contour map for the increment of $\ln(g)$ with the torsion, θ, and the wagging, α, angles. The increment is measured from the minimum of -10.5037. The map shows increments $* 10^3$.

select values of 0.01 Å and 0.001 deg for the increments Δq_i.

The kinetic coupling between wagging and methyl torsion is found to be important. In the case of the hydrogen wagging the small mass of the hydrogen atom produces a coupling constant about 60% the value of the methyl internal rotation constant. Thus, in the models describing internal rotation for molecules where the wagging plays an important role, excited states of carbonyl and thiocarbonyl compounds (Clouthier & Moule, 1989), it is necessary to take into account both motions for obtaining an accurate description of energy levels and consequently of thermodynamical properties.

The change of the kinetic constants as a function of the torsion and wagging angles is found to be small. This change seems to be small enough as to justify the use of constant values taken from the equilibrium geometry. This fact and the small variation of the G matrix determinant supports the use of equation (12) for the general treatment of large range vibrations.

Program availability—The program is available from QCPE (program number 629).

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