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FORCE CONSTANT CALCULATIONS USING THE "SIMPLEX" METHOD

APPLICATION TO IMIDAZOLIDINETRIONE (PARABANIC ACID)

Key Words : Infrared and Ramand spectroscopy - Force constants - "simplex" optimization - invariants of similarity of a GF matrix - Frequencies and potential energy distribution

L. Coclers, R. Bouché*, A. Vanclef**, R. Bontemps and C. Nielsen***

Service de Contrôle des Médicaments,

137, rue Stévin - B - 1040 BRUXELLES.

* Université Catholique de Louvain - Ecole de Pharmacie,

73, Av. E. Mounier - B - 1200 BRUXELLES.

** Faculté Polytechnique de Mons - B - 7000 MONS.

*** Department of Chemistry, University of Oslo -

OSLO 3 NORWAY.

ABSTRACTS

With the object to improve the results of least squares refinement of force constants the authors propose an iterative procedure using the "simplex" system and the invariants of similarity. These invariants are calculated by a special way

without determination of roots. This method has been applied with satisfaction to parabanic acid.

INTRODUCTION

A disadvantage of the commonly used least squares refinement of force constants from vibrational spectroscopic data is the lack of an objective comparative test during the optimization. Often, the comparative test consists only of matching the observed and calculated frequencies in in- or decreasing order. To overcome this problem, we have used as a comparative test the invariants of the GF-matrix (which have the same absolute values as the coefficients of the characteristic equation).

The invariants of the GF-matrix have been calculated without determining the eigenvalues and the F-matrix have been optimized by the "simplex" method of Spendley[1]. The "simplex" method has primaryly been applied to optimization problems in quantitative analytical chemistry[2] and in synthesis[3]. A survey and bibliography have been published by Massart[4]. The main advantage of the "simplex" method is that it seems to be always convergent in contrast to the usual least squares method, which often results in oscillating solutions.

As an example we have applied the "simplex" method to refining the force field for the in-plane vibrations of parabanic acid.

THEORETICAL DESCRIPTION

The "simplex" method of Spendley[1] is an optimization technique in which the independent parameters are varied according to a sequential design. The method is based on the evolution of a "simplex", a well-defined geometrical figure in the n-dimensional space. The evolution is done by geometrical scanning on the response surface, as described in the mathematical work on EVOP (Evolutionary operation) by Box[5].

If a system depends on n parameters, we begin with n+1 sets of these parameters according to a particular scheme. We have chosen the following scheme :

(example for 5 parameters)

0	0	0	0	0
1	0	0	0	0
1/2	1	0	0	0
1/2	1/3	1	0	0
1/2	1/3	1/4	1	0
1/2	1/3	1/4	1/5	1

In this scheme, 0 represents the original parameters while 1 1/2, 1/3, ... represents the unit or fractional increments for the parameters. From these n+1 sets of parameters we obtain n+1 responses. The set that results in the "worst" response is eliminated and replaced by a new set, derived from :

$$\frac{2 \times (\Sigma \text{ retained values of parameters})}{\text{number of parameters}} - \text{the rejected value}$$

We thus obtain a new set of parameters from which a new response is calculated. This response is in turn compared with the earlier calculated responses : the set which leads to the "worst" response is rejected, replaced according to the above equation, and so forth.

The evolution of the "simplex" can lead to a set of parameters found before. In this case, we have a so called "reflection back".
In order to overcome this dead-lock, the set of parameters corresponding to the second-worst response is rejected and replaced (keeping the set resulting in the worst response).

The best choice of response function is not obvious. As mentioned before, the sum of the deviations between observed and calculated frequencies is not an ideal comparative test. Instead, we prefer to use the invariants of the GF-matrix. Thus, the expression we have chosen as the "simplex" response is then given by the calculated invariants (S_C) and the observed invariants (S_R) :

$$R = \left[\frac{|S_C - S_R|}{|S_R|} \right]^n$$

with n = 1 in our case.

This formula makes abstraction of the dimensions giving the same importance to each invariants in the algebric sum.

The reference invariants are calculated from the selected experimental frequencies by a formula derivated from combinatory analysis ;

$$S_n = \frac{1}{n} \sum_{i=1}^{n} \left[(S_{n-i} \Sigma \lambda^i) \ (-(-1^i)) \right]$$

Where $S_o = 1$

S_n = sum of the roots to n.

λ^i = sum of the ith power of the roots.

The invariants of the GF-matrix have been calculated without determining the eigenvalues (see appendix). This method, easy and rapid for calculating the invariants of similarity (or characteristic equation coefficients), should be of interest in the physical chemistry, where one often must resolve the characteristic equation of a matrix system.

RESULTS AND DISCUSSION

An initial set of valence force constants for parabanic acid was with minor modifications transferred from maleimide[6]. In order to limit the number of parameters in the optimization procedure, we have constrained a number of interaction constants to be equal.

The experimental data were with a few modifications[7] taken from Coclers[8]. The modifications concern the $\nu_9(A_1)$ band at 337 cm^{-1}, the $\nu_{23}(B_2)$ band at 595 cm^{-1} and the $\nu_{24}(B_2)$ band at 430 cm^{-1}.

OBSERVED AND CALCULATED FREQUENCIES BEFORE THE "SIMPLEX" ITERATION

	Frequencies (cm^{-1})		
	Exp.	Calc.	Deviation (%)
A_1	3160	3148	0,4
	1825	1889	4
	1740	1864	7
	1342	1494	11
	1125	1314	17
	999	967	3
	804	855	6

	Frequencies (cm^{-1})		
	Exp.	Calc.	Deviation (%)
A_1	660	617	7
	337	361	7
B_2	3220	3147	2
	1777	1969	11
	1380	1601	16
	1360	1367	1
	982	1238	21
	755	709	6
	595	682	15
	430	396	8

INVARIANTS OBTAINED AFTER "SIMPLEX" ITERATION COMPARED WITH THE REFERENCE INVARIANTS *

A_1	Theoretical model invariants	Reference invariants (experim.origin)	% deviation
s_1	12,748	12,729	0,1
s_2	59,044	59,068	0,04
s_3	136,865	137,319	0,3
s_4	177,725	178,815	0,6
s_5	134,550	135,701	0,8
s_6	59,105	59,707	1
s_7	14,309	14,442	0,9
s_8	1,665	1,673	0,5
s_9	0,063	0,063	0,0

* The computer program of calculation can be obtained on request.

Most of the calculated invariants giving the best response, deviate less than 1 p.c. with the reference invariants. Ideally, the simplex should decrease to zero, but when the optimal response approaches, evolution becomes slow and the response remains in a stationnary zone (self defeating).

Furthermore, it must be kept in mind that the reference invariants and the GF mathematical model derive from experimental

CALCULATED FREQUENCIES AND MODES OF VIBRATION OBTAINED AFTER ITERATION COMPARED WITH THE EXPERIMENTAL ONE

Experim. (cm^{-1})	Calcul. (cm^{-1})	Deviation in p.c.	Calculated attribution*
Symmetric vibrations A_1			
3160	3181	1	$\nu NH(98)$
1825	1845	1	$\nu CO_I(34), \nu CO_{II}(17)\ \Delta(17)$
1740	1711	2	$\nu CO_{II}(22), \nu CN(25), \Delta(18), \nu CO_I(14)$
1342	1328	1	$\delta NH(36),\ \Delta(36)$
1125	1185	5	$\Delta(50)$
999	925	7	$\nu C\text{-}C(47),\ \Delta(26)$
804	820	2	$\nu C\text{-}N_I(25), \nu C\text{-}N_{II}(33), \nu C\text{-}C(33)$
660	664	1	$\nu C\text{-}N(32), \nu C\text{-}C(17),\ \Delta(17)$
337	339	1	$\nu C\text{-}C(46), \delta CO(21),\ \Delta(17)$
Antisymmetric vibrations B_2			
3220	3175	1	$\nu NH(99)$
1777	1846	4	$\nu CO_I(51),\ \Delta(31)$
1380	1394	1	$\nu CN_I(28), \nu CN_{II}(20), \delta\ NH(19)\delta CO(19)$
1360	1307	4	$\delta NH(88)$
982	996	1	$\nu CN_I(27), \nu CN_{II}(28), \delta CO(24)$
755	725	5	$\Delta(63)$
595	646	8	$\nu CN_I(39), \nu CN_{II}(26), \delta CO(27)$
430	401	7	$\delta CO(53)$

* The number represents the p.c. of the relatively large contribution (only those that represents more than 50 p.c. of the largest one).

FINAL FORCES VALUES

Stretching forces (mdyne $\mathring{A}^{-1}$)

K_{CO} (I) = 10,13 (O=C-C=O)

K_{CO} (II) = 8,76 (-N-C-N, C=O)

K_{NH} = 5,54

K_{CN}(I) = 6,08 (-N-C-C-)

K_{CN}(II) = 6,50 (-C-N-C-)

K_{C-C} = 4,98

Bending forces (mdyne $\mathring{A}$ rad^{-2})

H_{N-C-C} = 2,11

H_{C-N-C} = 2,04

H_{N-C-N} = 1,84

$H_{C-C=O}$ = 1,07

H_{C-N-H} = 0,45

Interaction forces (stret/stret : mdyne $\mathring{A}^{-1}$)
(stret/bend : mdyne rad^{-1})

$F_{CN/NC} = F_{CN/CC}$ = 2,35

$F_{CO/CO}$ = - 0,15

$F_{CO/CN} = F_{CO/CC}$ = 0,65

$F_{CN/CNN} = F_{CN/CNC} = F_{CC/CCN}$ = - 1,03

$F_{CN/NCO} = F_{CC/CCO}$ = - 0,15

$F_{CO/NCC} = F_{CO/NCN}$ = - 0,10

$F_{CN/CNH}$ = - 0,08 = - 0,08

B_2	Theoretical model invariants	Reference invariants (experim.origin)	% deviation
s_1	11,299	11,399	0,9
s_2	42,910	43,115	0,5
s_3	76,652	76,832	0,2
s_4	72,089	72,231	0,2
s_5	36,648	36,734	0,2
s_6	9,793	9,833	0,4
s_7	1,249	1,262	1
s_8	0,056	0,059	4,8

data with errors and that the potential function is not perfect.

The experimental frequencies are in good agreement with the calculated ones. We find well-definited groups : νNH, νCO, νCH. The symmetric and antisymmetric mode of νNH are almost pure. Those of νCO are combinated confirming that they are coupled. νCN are combinated with νCO and ω.

The Δ modes are generally more complex. In this zone of low frequencies, the frequency group concept disappears. The deviation between experimental and theoretical frequencies are a little greater : perhaps is it the consequence of neglected interactions.

From the values of stretching force constants, we see that the carbonyl between the 2 nitrogen is weaker and consequently this CO is more polar.

CONCLUSION

We propose an iterative procedure for the calculation of force constants from a GF matrix using the "simplex" system. Our optimization method uses invariants of similarity (coefficients of the characteristic equation of GF) as comparative test between theory and experiments. These invariants are calculated by a special way without determination of roots. This method has been applied with satisfaction to parabanic acid.

REFERENCES

1) W. SPENDLEY, G.R. HEXT, and F.R. HIMSWORTH.
Sequential Application of Simplex Design in Optimization and Evolutionary Operation.
Technometrics, 4 (4), 441 (1962).

2) S.L. MORGAN and S.N. DEMING.
Simplex Optimization on Analytical Chemical Methods.
Anal. Chem. 46 (9), 1170 (1974).

3) D.S. AMENTA, C.E. LAMB, and J.J. LEARY.
Simplex Optimization of Yield of sec-Butylbenzene in a Friedel-Crafts alkylation.
J. Chem. Educ., 56 (8), 557 (1979).

4) D.L. MASSART, A. DYKSTRA and L. KAUFMAN.
Evaluation and Optimization of laboratory methods and analytical procedures (the simplex method p. 267-277).
Elsevier Scientific Publication Company (1978).

5) G.E.P. BOX and K.B. WILSON.

On the experimental attainment of optimum conditions.

Journal of the Royal Statistical Society, BXIII, (1), 1 (1951).

6) T. WOLDBAEK, P. KLABOE and C.J. NIELSEN.

The Vibrational Spectra of Maleimide and N-D Maleimide.

J. Mol. Struct., 27, 283 (1975).

7) L. COCLERS.

Nouvelle méthode de calcul des constantes de forces interatomiques à partir des fréquences observées en spectrométrie infrarouge et Raman. Application à l'acide parabanique.

Thèse de doctorat en Sciences Pharmaceutiques (1979).

Université Catholique de Louvain - Faculté de Médecine.

8) L. COCLERS, A. VANCLEF and R. BOUCHE.

Study of the in-plane Vibrations of Imidazolidinetrione.

Spectrosc. Lett., 11 (10), 799 (1978).

APPENDIX

A matrix can be subjected to a similarity transformation. For any given square matrix the number of equivalent matrix is unlimited, all of them being related by similarity transformation.

B is similar to A if we have the relation :

$$B = C^{-1} AC.$$

Where C is the transformation matrix from A to B. Similar matrices have the same characteristic equations.

A particular similar matrix can be derived from the coefficients of the characteristic equation of a matrix.

From a nth order matrix, with the characteristic equation (in polynominal form)

$$\lambda^n + \sigma_1\lambda^{n-1} + \sigma_2\lambda^{n-2} + \ldots + \sigma_{n-1}\lambda + \sigma_n = 0$$

($-\sigma_1$ is the trace of the matrix and $(-1)^n\sigma_n$ the determinant of the matrix).

The similar matrix formed only of the coefficients will be :

$$\Sigma = \begin{bmatrix} 0 & 0 & 0 & 0 & \ldots & 0 & 0 & -\sigma_n \\ 1 & 0 & 0 & 0 & \ldots & 0 & 0 & -\sigma_{n-1} \\ 0 & 1 & 0 & 0 & \ldots & 0 & 0 & -\sigma_{n-2} \\ . & . & . & . & \ldots & . & . & \\ . & . & . & . & \ldots & . & . & \\ 0 & 0 & 0 & 0 & \ldots & 1 & 0 & -\sigma_2 \\ 0 & . & . & . & \ldots & 0 & 1 & -\sigma_1 \end{bmatrix}$$

Example :

Matrix A.

$$A = \begin{bmatrix} 0 & 7 & -6 \\ -1 & 4 & 0 \\ 0 & 2 & -2 \end{bmatrix}$$

Characteristic equation.

$$\begin{vmatrix} 0-\lambda & 7 & -6 \\ -1 & 4-\lambda & 0 \\ 0 & 2 & -2-\lambda \end{vmatrix} = 0$$

$$\lambda^3 - 2\lambda^2 - 1\lambda + 2 = 0$$

$$(\sigma_1 = -2,\ \sigma_2 = -1,\ \sigma_3 = +2)$$

Σ matrix.

$$\Sigma = \begin{bmatrix} 0 & 0 & -2 \\ 1 & 0 & +1 \\ 0 & 1 & +2 \end{bmatrix}$$

We can verify : $|A - \lambda I| = |\Sigma - \lambda I|$

Between a matrix A and its Σ matrix, we have the similarity relation :

$$Q^{-1} \Sigma Q = A \qquad (1).$$

Where Q is the transformation matrix from Σ to A. This relatic can be put on the equivalent form :

$$Q A = \Sigma Q \qquad (2)$$

A and Σ being similar have same characteristic equation and also same eigenvalues.

So $$A L_a = L_a \Lambda \qquad (3)$$

$$\Sigma L_\sigma = L_\sigma \Lambda \qquad (4)$$

where

L_a = eigenvectors of A;

L_σ = eigenvectors of Σ;

Λ = eigenvalues of A and Σ.

Postmultiplying (2) by L_a :

$$Q\ A\ L_a = \Sigma\ Q\ L_a \qquad (5)$$

Premultiplying (3) by Q :

$$Q\ A\ L_a = Q\ L_a\ \Lambda \qquad (6)$$

From (5) and (6) we see that :

$$\Sigma\ Q\ L_a = Q\ L_a\ \Lambda \qquad (7)$$

Comparing (7) with (4) we see that :

$$Q\ L_a = L_\sigma \qquad (8)$$

From this last relation, we have imagine to impose that the last row of Q have all elements equal to zero except the last one. In fact, we can put all the elements of the last row of L_a and L_σ to 1 because they are eigenvectors matrices from which each vector is not completely definited (an eigenvector can be multiplied by any scalar factor k).

$$\begin{bmatrix} \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 1 & 1 & 1 & \cdots & 1 \end{bmatrix} = \begin{bmatrix} \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix} \times \begin{bmatrix} \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 1 & 1 & 1 & \cdots & 1 \end{bmatrix}$$

$$L_\sigma \qquad = \qquad Q \qquad\qquad L_a$$

With this particular last row of Q, all other rows can be derived easily.

It can be demonstrated that all the elements of Q can be derived from the original matrix A and the matrix Σ from the relation $QA = \Sigma Q$ equaling all terms of the two consequent matrices of multiplication.

This lead us to a supplementary row of Q in which all elements are zero. Example :

$$\begin{bmatrix} 12 & 27 & 17 & 116 \\ -2 & -5 & -3 & -108 \\ -4 & -8 & -5 & 84 \\ 1 & 2 & 1 & 8 \end{bmatrix}$$

We transpose A and multiply by the column vector (0,0,0,1). To the new resulting vector, we add σ_1 to the last term; A' is multiplied by the new vector and so on. To all last terms of each vector, we add respectively σ_2, σ_3 ... Each column vector represents a row of Q.

$$\begin{bmatrix} 12 & -2 & -4 & 1 \\ 27 & -5 & -8 & 2 \\ 17 & -3 & -5 & 1 \\ 116 & -108 & 84 & 8 \end{bmatrix} \times \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} + \begin{bmatrix} 1 \\ 2 \\ 1 \\ 8 + \sigma_1 \end{bmatrix}$$

$$\rightarrow\begin{bmatrix} 12 + 1\,\sigma_1 \\ 25 + 2\,\sigma_1 \\ 14 + 1\,\sigma_1 \\ 48 + 8\,\sigma_1 + \sigma_2 \end{bmatrix} \rightarrow \begin{bmatrix} 86 + 12\,\sigma_1 + 1\,\sigma_2 \\ 183 + 25\,\sigma_1 + 2\,\sigma_2 \\ 107 + 14\,\sigma_1 + 1\,\sigma_2 \\ 252 + 48\,\sigma_1 + 8\,\sigma_2 + \sigma_3 \end{bmatrix}$$

$$\rightarrow\begin{bmatrix} 490 & 86\sigma_1 & 12\sigma_2 & 1\sigma_3 \\ 1055 & 183\sigma_1 & 25\sigma_2 & 2\sigma_3 \\ 630 & 107\sigma_1 & 14\sigma_2 & 1\sigma_3 \\ 1216 & 252\sigma_1 & 48\sigma_2 & 8\sigma_3 + \sigma_4 \end{bmatrix} \rightarrow \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

If σ_1, σ_2, σ_3, σ_4 are unknown, we can derive the system of linear equations :

$$\begin{bmatrix} 86\sigma_1 + 12\sigma_2 + 1\sigma_3 + 0\sigma_4 \\ 183\sigma_1 + 25\sigma_2 + 2\sigma_3 + 0\sigma_4 \\ 107\sigma_1 + 14\sigma_2 + 1\sigma_3 + 0\sigma_4 \\ 252\sigma_1 + 48\sigma_2 + 8\sigma_3 + 1\sigma_4 \end{bmatrix} = \begin{bmatrix} - 490 \\ - 1055 \\ - 630 \\ - 1216 \end{bmatrix}$$

Which has the form of : $P'X = - R$.

and from which we calculate : $X = \left[P'^{-1}\right]\left[- R\right]$

In this case : $\sigma_1 = - 10$, $\sigma_2 = + 35$, $\sigma_3 = - 50$, $\sigma_R = + 24$ and the characteristic equation :

$$\lambda^4 - 10\lambda^3 + 35\lambda^2 - 50\lambda + 24 = 0$$

If we calculate the eigenvalues of the initial matrix, we find :

$$\lambda_1 = 1,\ \lambda_2 = 2,\ \lambda_3 = 3,\ \lambda_4 = 4$$

The invariants are :

$$\lambda_1 + \lambda_2 + \lambda_3 + \lambda_4 = 10$$

$$\lambda_1 \lambda_2 + \lambda_1 \lambda_3 + \lambda_1 \lambda_4 + \lambda_2 \lambda_3 + \lambda_2 \lambda_4 + \lambda_3 \lambda_4 = 35$$

$$\lambda_1 \lambda_2 \lambda_3 + \lambda_1 \lambda_2 \lambda_4 + \lambda_1 \lambda_3 \lambda_4 + \lambda_2 \lambda_3 \lambda_4 = 50$$

$$\lambda_1 \lambda_2 \lambda_3 \lambda_4 = 24$$

and the characteristic equation :

$$\lambda^4 - 10\lambda^3 + 35\lambda^2 + 50\lambda + 24 = 0$$

which is the same as that found in the system of linear equations.

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