Asian Journal of Chemistry Vol. 2, No. 3 (1990), 302-307

Vibrational Analysis of Formic Acid

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Force constants of HCOOH and DCOOD involving seventh and second order vibrational problems have been calculated by the method of kinetic constants in conjunction with a new technique of solving the secular equation. The non-linear equations are solved by the Newton-Raphson iterative method, where the values of functions and derivatives are obtained using the new technique exploiting the symmetry in the secular equation. The other molecular constants like mean square amplitudes vibration and Coriolis coupling constants are also calculated.

INTRODUCTION

The molecules HCOOH and DCOOD belong to the C_s point group with the frequency distribution $7A'$ (in-plane) and $2A''$ (out-of-plane) vibrations. The A'' vibration mode is an out-of-plane bending vibrational one. All the vibrations are active both in infrared and Raman spectra. The molecular parameters and frequencies of HCOOH obtained from microwave and infrared spectra by Millikan and Pitzer[1] are used in the computation of the potential constants.

THE METHOD OF KINETIC CONSTANTS

The kinetic constant method[2] gives a relation between the potential constants, F_{ij} and kinetic constants, k_{ij} as

$$\frac{F_{ij}}{F_{jj}} = \frac{k_{ij}}{k_{ji}} \, (i < j)$$

This relation enables one to express the $n(n-1)/2$ off-diagonal force constants in terms of the n diagonal force constants. Thus the problem of indeterminancy is overcome. Then it remains to solve for the diagonal force constants using the secular equation which yields n non-linear equations in n unknowns. In solving the non-linear equations, Newton-Raphson's iterative procedure is used and here a new technique is adopted in the determination of the values of functions and derivatives for a set of unknown values.

Newton-Raphson Iterative Method

Newton-Raphson method consists in assuming an initial set of values for unknowns, substituting them in the non-linear equations and checking how far they satisfy them. The increments for each unknown is then calculated using expressions, involving the determinants consisting of values of functions of equations and their derivatives with respect to the unknowns. These increments are then added to the corresponding unknowns and new set of values for unknowns are obtained and the process of putting them back into the equations is continued followed by the calculation of further increments until the required accuracy is obtained.

So the iterative method involves mainly the calculation of the values of the functions and their derivatives at the corresponding points. Here a new general procedure is developed to obtain these values of functions and derivatives in a unique way using the symmetry in the secular equation. This is explained below.

Second Order Problem

In a second order problem, the secular equation leads to the following two equations, one of first degree and other of second degree in F_{ij}

$$f_1 \equiv H_{11} + H_{22} - (\lambda_1 + \lambda_2) = 0$$

$$f_2 \equiv \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} - (\lambda_1 \cdot \lambda_2) = 0$$

Here $H \equiv GF$ and $|GF - \lambda E| = 0$ becomes $|H - \lambda E| = 0$. The elements of H are given by

$$H_{ij} = G_{1i}F_{1j} + G_{2i}F_{2j} \quad (i = 1, 2; j = 1, 2)$$

Using these expressions for H_{ij} the derivatives are obtained as

$$\frac{\partial f_1}{\partial F_{11}} = G_{11} \quad \text{and} \quad \frac{\partial f_1}{\partial F_{22}} = G_{22}$$

$$\frac{\partial f_2}{\partial F_{11}} = \begin{vmatrix} G_{11} & H_{12} \\ G_{12} & H_{22} \end{vmatrix} \quad \text{and} \quad \frac{\partial f_2}{\partial F_{22}} = \begin{vmatrix} H_{12} & G_{12} \\ H_{21} & G_{22} \end{vmatrix}$$

The General $n \times n$ Problem

When this is extended to a 3×3, 4×4 and other higher order problems, a certain symmetry is observed in the functions and their derivatives which can be utilized to calculate them. The function f_i consists of the difference between the sum of all the principal minors of order i of the matrix H and a similar sum for a diagonal matrix Λ having λ_i on their diagonals. The sum of all the principal minors of various orders can be directly obtained from the characteristic equation of the corresponding matrices.

The derivatives of f_i with respect to F_{kk} are determined as the sum of all principal minors of order i involving H'_{kk} only, where H' is the matrix obtained by replacing the kth column of H by the kth column of G matrix. To obtain them, the sum of the principal minors of order i in H matrix is determined and from this the sum of the principal minors of order i in a truncated H-matrix (leaving out the kth row and kth column) is subtracted.

The advantage of this general procedure is that it can be applied directly to a general nth order problem and there is no limitation in its extension to a general $n \times n$ case.

Other Molecular Constants

Utilising Cyvin's[3] equation $\Sigma = L \Delta \tilde{L}$, the symmetrized mean square amplitude quantities for bonded atom-pairs are calculated at 298 K. From these values, the valence mean square amplitudes of vibration and hence the mean amplitudes of vibration are determined.

The Coriolis matrix elements (c^{α}) are obtained by the vector method of Meal and Polo[4]. The ζ^{α} elements are evaluated from the c^{α} matrix using the relation

$$\zeta^{\alpha} = L^{-1} c^{\alpha} \tilde{L}^{-1}$$

where L is the transformation matrix between normal and symmetry co-ordinates.

The Coriolis sum rules for both $A' \times A'$ and $A' \times A''$ types of coupling for the present type of molecules are given below.

$$\sum_{i=1 \text{ to } 7} (\zeta_{ij}^{\alpha})^2 = 1 \quad j = 8, 9; \alpha = x, y$$

$$\sum_{\substack{i=1 \text{ to } 7 \\ j=1 \text{ to } 7}} (\zeta_{ij}^{z})^2 = 3 \quad (i < j)$$

RESULT AND DISCUSSION

The general quadratic valence force field has been used in the present study of force constants for HCOOH and DCOOD. The force constants and compliance constants determined here are listed in Table 1 and 2. The C–H stretching force constant (F_{33} = 4.76 mdyn/Å) agrees well with the corresponding value obtained earlier by Gnanasekaran et al.[5] (4.88 mdyn/Å) for CH_3HgCCH. The O–H′, C–O and C=O stretching force constants assume higher values when compared to that of C–H stretch. The force constant for COH, H′CO, O′CO bends (0.050 mdyn/Å, 0.95 mdyn/Å and 0.85 mdyn/Å) are very much lesser compared to those of stretching force constants. The out-of-plane bending force constants f_{γ} and f_{δ} are very low in both the cases. This is perhaps due to the lower steric hindrance for out-of-plane bending motions which would lower the force constant values.

The compliance constants are the inverse of the force constants as introduced[6] by Jones ($N = F^{-1}$ and $n = f^{-1}$). A primary (or diagonal) compliance constant is a measure of the displacement in a coordinate as a result of a force imposed on this coordinate if all other coordinates are allowed to adjust themselves to minimise the energy. The off-diagonal

TABLE 1

PRINCIPAL FORCE CONSTANTS (in mdyne/Å) AND COMPLIANCE CONSTANTS (in mdyne^{-1} Å)

Mode	F_{ij}	HCOOH	DCOOD	N_{ij}	HCOOH	DCOOD
			A′ Species			
O–H′ stretch	F_{11}	7.12	7.29	N_{11}	0.14	0.14
C–O stretch	F_{22}	7.65	7.09	N_{22}	0.18	0.18
C–H stretch	F_{33}	4.76	5.02	N_{33}	0.21	0.20
C=O′ stretch	F_{44}	14.22	13.79	N_{44}	0.08	0.08
COH bend	F_{55}	0.50	0.66	N_{55}	1.81	1.70
H′CO bend	F_{66}	0.95	0.85	N_{66}	1.07	1.21
O′CO bend	F_{77}	0.85	0.85	N_{77}	1.35	1.25
			A″ Species			
out of plane bend, γ	F_{88}	0.30	0.30	N_{88}	3.45	3.48
torsion, δ	F_{99}	0.14	0.14	N_{99}	7.53	7.63

TABLE 2

INTERACTION FORCE CONSTANTS (in mdyne/Å) AND COMPLIANCE CONSTANTS (in mdyne^{-1} Å)

F_{ij}	HCOOH	DCOOD	N_{ij}	HCOOH	DCOOD
			A′ Species		
F_{12}	0.02	0.07	N_{12}	−0.00	0.00
F_{13}	0.05	0.09	N_{13}	0.00	0.00
F_{14}	0.12	0.20	N_{14}	0.00	0.00
F_{15}	0.01	0.04	N_{15}	0.00	0.00
F_{16}	0.06	0.09	N_{16}	0.01	−0.01
F_{17}	−0.03	−0.04	N_{17}	−0.01	0.01
F_{23}	0.05	0.07	N_{23}	0.00	0.00
F_{24}	3.27	2.59	N_{24}	−0.04	−0.03
F_{25}	0.47	0.91	N_{25}	−0.04	−0.04
F_{26}	0.23	0.31	N_{26}	−0.03	−0.06
F_{27}	0.76	0.60	N_{27}	−0.13	−0.13
F_{34}	0.25	0.48	N_{34}	0.00	−0.01
F_{35}	0.01	0.01	N_{35}	0.00	0.01
F_{36}	−0.16	−0.16	N_{36}	0.04	0.04
F_{37}	−0.07	−0.09	N_{37}	0.02	0.03
F_{45}	0.10	0.20	N_{45}	0.02	0.00
F_{46}	0.02	0.01	N_{46}	0.00	0.01
F_{47}	0.66	0.48	N_{47}	−0.03	−0.02
F_{56}	−0.01	−0.01	N_{56}	0.06	0.01
F_{57}	0.10	0.14	N_{57}	−0.19	−0.22
F_{67}	−0.01	−0.02	N_{67}	0.04	0.09
			A″ Species		
F_{89}	−0.03	−0.04	N_{89}	0.65	0.91

TABLE 3

MEAN AMPLITUDES OF VIBRATION AT 298 K (Å)

1(X–Y)	HCCOH	DCOOD	Ref (1)	Ref (1)*
1(O–H′)	0.071	0.071	0.071	0.068
1(C–O)	0.046	0.045	0.047	0.042
1(C–H)	0.079	0.067	0.079	0.077
1(C–O′)	0.037	0.037	0.039	0.032

*Experimental values

TABLE 4

CORIOLIS COUPLING CONSTANTS

ζ^{x}_{ij}	HCOOH	DCOOD	ζ^{y}_{ij}	HCOOH	DCOOD	ζ^{z}_{ij}	HCOOH	DCOOD
ζ_{18}	0.074	0.159	ζ_{18}	0.021	0.039	ζ_{12}	0.020	0.349
ζ_{28}	0.063	−0.104	ζ_{28}	0.396	−0.375	ζ_{13}	−0.006	−0.018
ζ_{38}	0.846	0.845	ζ_{38}	0.299	0.253	ζ_{14}	−0.083	−0.063
ζ_{48}	0.402	0.355	ζ_{48}	−0.441	−0.473	ζ_{15}	0.920	0.887
ζ_{58}	−0.004	−0.042	ζ_{58}	−0.226	0.260	ζ_{16}	−0.126	0.069
ζ_{68}	0.260	0.258	ζ_{68}	−0.644	−0.623	ζ_{17}	0.169	0.227
ζ_{78}	0.213	0.237	ζ_{78}	0.305	0.339	ζ_{23}	−0.090	0.153
ζ_{19}	0.886	0.853	ζ_{19}	0.255	0.237	ζ_{24}	−0.469	0.458
ζ_{29}	0.002	−0.196	ζ_{29}	0.448	0.117	ζ_{25}	0.128	−0.211
ζ_{39}	−0.213	−0.299	ζ_{39}	−0.088	−0.138	ζ_{26}	−0.073	0.044
ζ_{49}	0.239	0.243	ζ_{49}	−0.152	−0.110	ζ_{27}	−0.424	0.500
ζ_{59}	−0.293	−0.208	ζ_{59}	0.792	0.814	ζ_{34}	−0.274	−0.262
ζ_{69}	−0.058	−0.137	ζ_{69}	0.173	0.433	ζ_{35}	−0.229	0.034
ζ_{79}	0.152	0.155	ζ_{79}	0.218	0.222	ζ_{36}	−0.903	−0.915
						ζ_{37}	0.184	0.248
						ζ_{45}	−0.167	0.114
						ζ_{46}	0.150	0.202
						ζ_{47}	0.631	0.620
						ζ_{56}	−0.012	−0.068
						ζ_{57}	0.210	−0.046
						ζ_{67}	−0.345	−0.295

compliance constants are perhaps easier to define in a physical sense than the corresponding force constants as discussed by Jones[6]. The compliance constants are used in calculating the interaction coordinates of the type, $(l)_k = n_{lk}/n_{kk}$. Using these coordinates it is possible to determine the amount of stretching (or) contraction of the bonds for minimum energy configuration, when one particular bond is stretched. From Table 1, it is noted that the stretching compliance constants are always lesser than the bending compliance constants for both inplane and out-of-plane bending.

The mean amplitudes of vibration at 298 K are given in Table 3. It is seen that the mean amplitudes of vibration l(O–H′), l(C–O), l(C–H) and l(C–O′) are almost the same for the pair of isotopically substituted molecules. The mean amplitudes of vibration are compared with both experimental and theoretical values as shown in Table 3. The Coriolis coupling constants determined for these molecules are reported in Table 4. The larger values obtained for some of these constants suggest that the coupling between the concerned vibrational modes are stronger. The zeta constants obey the sum rules mentioned earlier.

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[*Received*: 10 May 1989; *Accepted*: 10 November 1989] AJC-111