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NOTES

Four Different Methods as Applied to 5×5 Order in AXYZ Type Molecules

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The potential energy constants of hydrogen isocyanate (HNCO) and its isotopically substituted molecule (DNCO) are calculated on the basis of General Valence Force Field. The interaction coordinates, coriolis coupling constants and rotational distortion constants of the molecules are also computed by four different methods and presented in this paper.

The quasi linear AXYZ type molecules belong to the C_S point group having six distinct normal modes of vibrations which fall under the irreducible representation $5A' + A''$. The A'' vibrational mode is an out-of-plane bending one. All the vibrational modes are active both in infrared and Raman spetra.

In the present study an attempt is made to calculate the force constants, iteration coordinates and other molecular constants involved in this fifth order vibrational problem by four different methods viz.

1. Isotani's method[1]. 2. L-Matrix approximation[2,2].
3. Herranz and Castano' method[4]. 4. Kinetic constant method[5,6].

Method 1: Based on a detailed analysis and physical reasoning, Isotani has suggested a method for determining the off diagonal force constant for a 2×2 vibrational problem. The diagonal force constants are then determined using the secular equation. It has further been suggested that this method can be extended to higher order vibrational problems by taking the various pairs of modes.

An $n \times n$ problem has been solved by first finding the $n(n-1)$ off diagonal force constants. Using these off diagonal force constants, the remaining n diagonal force constants are determined by using the Newton-Raphson iteration method of solving the n nonlinear equations in n unknowns.

Methods 2, 3 and 4: These methods have been used previously by many authors for the calculation of force constants and other molecular constants.

The iteration coordinates are obtained from the compliance constants which are inverse of the force constants. These coordinates have been introduced by Jones,[7,8] as a means of correlating the electronic struc-

ture with the bonding properties. The interaction coordinates give a qualitative picture of the changes in the electronic configurations accompanying a constrained displacement of the coordinate concerned. These coordinates have been calculated as ratios of compliance constants for various molecules.

Coriolis vibration rotation constants $\zeta_{ij}^{\alpha}(\alpha = x,y,z)$ in this type of molecules arise from the coupling $A' \times A'$ and $A' \times A''$. The Coriolis matrix elements $C_{ij}^{\alpha}(\alpha = x,y,z)$ are obtained by the vector method of Meal and Polo[9]. The ζ^{α} matrices are related to the C^{α} matrices as

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

The structural parameters and the vibrational frequencies used in the present work are taken from References[10]. Table 1 gives the valence force constants obtained using G.V.F.F. The H-N, D-N stretching force constants are nearly the same in this isotopic pair. The C=O & C=N stretching force constants assume higher values compared to that of H-N. The out-of-plane bending force constants f_{δ} is low in both the cases. Generally

TABLE 1

VALENCE FORCE CONSTANTS (in mdyne/Å)

f_{ij}	HNCO				DNCO			
	PW1	PW2	PW3	PW4	PW1	PW2	PW3	PW4
f_R	6.983	6.932	7.003	6.932	7.333	7.295	7.451	7.298
f_n	13.359	14.264	14.420	14.326	13.101	14.083	14.522	14.200
f_d	15.590	14.676	14.872	14.872	15.252	14.336	14.527	14.206
f_{α}	0.281	0.268	0.290	0.268	0.423	0.430	0.505	0.430
f_{ϕ}	0.517	0.460	0.479	0.460	0.372	0.322	0.360	0.322
f_{δ}	0.566	0.566	0.566	0.566	0.458	0.458	0.458	0.458
f_{Rn}	1.030	0.596	1.146	0.603	1.110	1.111	1.761	1.156
f_{Rd}	0.037	0.059	0.348	0.604	0.010	0.127	0.560	0.122
$f_{R\alpha}$	0.278	0.015	0.130	0.011	0.205	0.050	0.274	0.035
$f_{R\phi}$	−0.317	−0.018	−0.298	−0.018	−0.151	−0.019	−0.327	−0.019
f_{nd}	1.382	1.367	1.469	1.369	1.504	1.503	1.690	1.500
$f_{n\alpha}$	0.255	0.161	0.546	0.160	0.301	0.270	0.948	0.264
$f_{n\phi}$	−0.684	0.039	0.169	0.039	−0.691	0.047	0.299	0.047
$f_{d\alpha}$	−0.004	0.092	0.106	0.091	0.027	0.154	0.217	0.150
$f_{d\phi}$	0.196	0.022	0.038	0.022	0.179	0.027	0.074	0.027
$f_{\alpha\phi}$	0.069	0.080	0.108	0.080	0.070	0.095	0.174	0.095

R—M-N stretch γ—N=C stretch d—C=O stretch
α—HNC bend ϕ—NCO linear bend δ—out-of-plane bend
PW—present work.

the diagonal force constants are almost same for HNCO and its isotopically substituted molecules and the values computed by four different methods in good agreement.

A study of interaction coordinates is given in Table 2, to reveal certain interesting features relating to molecular vibrations satisfying the principle of minimisation of energy. By taking HNCO molecule as an example a few cases are discussed below.

TABLE 2

INTERACTION COORDINATES

	HNCO				DNCO			
	PW1	PW2	PW3	PW4	PW1	PW2	PW3	PW4
$(r)_R$	−0.012	−0.041	−0.041	−0.041	−0.500	−0.072	−0.092	−0.079
$(d)_R$	−0.006	0.000	−0.013	0.000	0.000	0.000	−0.019	0.000
$(\alpha)_R$	−1.167	−0.041	−0.615	−0.027	−0.514	−0.086	−0.827	−0.050
$(\phi)_R$	0.754	0.048	0.788	0.048	0.407	0.094	1.384	0.086
$(R)_n$	−0.023	−0.084	−0.120	−0.084	−0.077	−0.136	−0.175	−0.152
$(d)_n$	−0.107	−0.084	−0.080	−0.080	−0.111	−0.095	−0.075	−0.097
$(\alpha)_n$	−1.261	−0.563	−1.800	−0.563	−1.011	−0.575	−1.687	−0.569
$(\phi)_n$	1.523	0.014	−0.013	0.014	1.066	0.013	−0.162	0.013
$(R)_d$	−0.015	0.000	−0.029	0.000	0.000	0.000	−0.042	0.000
$(r)_d$	−0.138	−0.088	−0.088	−0.086	−0.144	−0.100	−0.085	−0.098
$(\alpha)_d$	0.338	−0.294	−0.161	−0.259	0.179	−0.300	−0.185	−0.281
$(\phi)_d$	−0.630	0.000	−0.029	0.000	−0.820	0.014	−0.071	0.014
$(R)_\alpha$	−0.045	−0.001	−0.022	−0.001	−0.027	−0.004	−0.045	−0.002
$(r)_\alpha$	−0.026	−0.010	−0.032	−0.010	−0.016	−0.016	−0.049	−0.016
$(d)_\alpha$	0.005	0.005	−0.002	−0.005	0.004	−0.008	−0.004	−0.007
$(\phi)_\alpha$	−0.198	−0.174	−0.227	−0.174	−0.268	−0.292	−0.476	0.292
$(R)_\phi$	0.050	0.003	0.050	0.003	0.017	0.003	0.058	0.003
$(r)_\phi$	0.055	0.000	0.000	0.000	0.057	0.000	−0.003	0.000
$(d)_\phi$	−0.017	0.060	0.000	0.000	−0.017	0.000	−0.001	0.000
$(\alpha)_\phi$	−0.348	−0.301	−3.393	−0.301	−0.215	−0.222	−0.364	−0.222

1. $(r)_R = -0.012$. That is, if $\Delta R = x$Å, $\Delta r = -0.012x$ Å or if R is stretched by x Å, r contracts by $0.012x$ Å.

2. $(\alpha)_\phi = -0.348$. That is, if $\sqrt{r}R\ \Delta\phi = x$ Å=radian, then $\sqrt{r}R$

$\Delta\alpha = -0.348 \times$ Å $-$radians. This means that if ϕ changes by x radians, α decreases by $0.348\sqrt{(r/R)}$ radians. The important first order Coriolis coupling constants are those of the A′×A′ type with respect to z-axis which are listed in Table 3. The centrifugal distortion constants are presented in Table 4. The values of D_J, D_K and D_{JK} for both molecules show a distinct trend in all the four methods. All the four methods give almost similar values of centrifugal distortion constants, indicating

TABLE 3

CORIOLIS COUPLING CONSTANTS WITH RESPECT TO Z AXIS

ξ	HNCO				DNCO			
	PW1	PW2	PW3	PW4	PW1	PW2	PW3	PW4
Coupling A′×A′ (along z-axis)								
$\xi_{1,2}$	−0.003	−0.079	0.077	−0.080	0.052	−0.109	0.100	−0.112
$\xi_{1,3}$	−0.136	−0.147	−0.028	−0.148	−0.200	−0.204	−0.049	−0.205
$\xi_{1,4}$	0.948	0.943	0.973	−0.943	0.895	0.903	0.955	−0.898
$\xi_{1,5}$	−0.243	0.248	0.158	0.247	−0.350	0.310	0.181	0.319
$\xi_{2,3}$	0.081	0.000	0.002	0.000	0.081	0.000	0.004	0.002
$\xi_{2,4}$	0.252	−0.254	−0.161	0.255	0.372	−0.327	−0.190	0.337
$\xi_{2,5}$	0.963	0.963	0.986	0.963	0.922	0.938	0.981	0.934
$\xi_{3,4}$	−0.157	−0.129	−0.161	0.128	−0.171	−0.161	−0.221	0.159
$\xi_{3,5}$	−0.001	−0.063	−0.034	−0.067	−0.044	−0.104	−0.059	−0.112
$\xi_{4,5}$	−0.021	0.075	−0.008	−0.075	−0.072	0.100	−0.012	−0.101

TABLE 4

CENTRIFUGAL DISTORTION CONSTANTS (in MHz)

Molecule	D_J	D_K	D_{JK}	R_5	$-R_6$	δ_J	Method
HNCO	0.041	37497.0	153.520	7.960	0.006	0.024	1
	0.038	34851.0	149.380	9.219	0.005	0.002	2
	0.034	32505.0	145.620	10.944	0.004	0.022	3
	0.038	34778.0	149.270	9.242	0.005	0.022	4
DNCO	0.040	3407.2	39.440	1.004	0.005	0.023	1
	0.034	2983.0	37.366	1.806	0.004	0.019	2
	0.028	2464.2	35.299	2.684	0.003	0.014	3
	0.034	2976.3	37.336	1.808	0.004	0.019	4

the validity of these methods. The order of magnitude of these constants is very considerable, but all the four methods give values in the same close range.

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