On the Applicability of Redington's Method of Determination of Force Field to Bent XYZ Type Systems

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Force fields of NSF, NSCl, NSBr, SSO, HCO, HOF, HOCl, HOBr and HOI have been computed using Redington's method. The angle parameters φ_{12}, φ_{13} and φ_{23} are fixed through F_{steep} critical point solution. The parametrised eigenvector matrices obtained are found to possess the properties predicted by Peacock et al. Mean amplitudes of vibration, Coriolis coupling constants, inertia defects and centrifugal distortion constants have also been calculated and compared with literature values. Redington's approach is found to reproduce all the molecular constants with accuracies comparable with conventional methods.

Introduction

The parametric representation method of force field computation consists mainly in the determination of $n(n-1)/2$ angle parameters, where n is the order of the problem. The three angle parameters of a (3×3) order problem can be fixed using either one or more of the experimentally observed data such as isotopic frequencies, Coriolis coupling constants and centrifugal distortion constants [1—3]. Redington and Aljibury [4] proposed a method which needs only the fundamental frequencies for the evaluation of molecular constants. In this method the parameters are fixed by finding the critical points of a function called F_{steep}. This has been extensively applied to some X_2Y_4 [5], XY_4Z_2 [6], XY_3Z [7] and XY_3Z_2 [8] type molecules. In all these papers it is observed that the molecular constants are reproduced with reasonable accuracy by a single angle parameter in a three dimensional problem. Also, Redington and Aljibury [4] have applied only the "F_{steep} intersection" solution, an additional possibility of finding the angle parameters, to XYZ C_s point group molecules. In the present work an attempt has been made to determine the three angle parameters and hence the molecular constants of bent XYZ type systems through "F_{steep} critical point" solution.

Theoretical Consideration

Expressions for the parametrised form of the force constant matrix F, the F_{steep} function and the restoring force constant F_k are given by Redington and Aljibury [4] along with the suggestion of maximisation of F_k corresponding to the highest frequency to fix the locale of the true F_{steep} critical point. For F_k to assume its maximum value the condition to be satisfied is,

$$\frac{\partial}{\partial \varphi_{ij}} (D_{\text{kk}}^{-1/2}) = 0\,, \tag{1}$$

where D_{kk}'s are the cofactors of the diagonal elements of F matrix.

In the present work some constants have been derived and expressions for tan φ_{ij}'s in terms of the constants obtained, thereby simplifying the procedure. Expansion of the expression for F with the free parameters φ_{12} leads to,

$$D_{kk} = P^2 \Lambda_1 \Lambda_2 + (Q S_{\varphi_{12}} + R C_{\varphi_{12}})^2 \Lambda_2 \Lambda_3 + (Q C_{\varphi_{12}} - R S_{\varphi_{12}})^2 \Lambda_3 \Lambda_1\,, \tag{2}$$

where C and S stand for the cosine and sine values of φ_{12} and

$$\begin{aligned} &R, Q, P = (-1)^{i+j} \mathscr{L}^0_{ij}\,, \\ &\quad i = 1, 2, 3 \text{ for } R, Q, P \text{ respectively,} \\ &\quad j = 1, 2, 3 \text{ for } K = 1, 2, 3 \text{ respectively.} \end{aligned} \tag{3}$$

$\mathscr{L}^0_{ij}$ is the cofactor of the element L^0_{ij} of the inverse of the initial eigen vector matrix L_0. Substitution for D_{kk} in Eq. (1) from Eq. (2) and further simplification results in a quadratic equation in tan φ_{12}. The solutions of this equation are,

$$\tan \varphi_{12} = Q/R \quad \text{and} \quad -R/Q\,. \tag{4}$$

Of these two values of φ_{12}, the one that gives higher value for F_k fixes the locale of the true F_{steep} critical point. The F_{steep} critical point in this location is found out. The corresponding angle is the true free parameter φ_{12}.

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For φ_{13},

$$D_{kk} = Q^2 \Lambda_3 \Lambda_1 + (R S_{\varphi_{13}} + P C_{\varphi_{13}})^2 \Lambda_1 \Lambda_2 + (R C_{\varphi_{13}} - P S_{\varphi_{13}})^2 \Lambda_2 \Lambda_3 . \quad (5)$$

The constants R, Q and P are calculated from the L_0^{-1} matrix constrained by φ_{12}, using Equation (3). The solutions of the quadratic equation obtained from Eq. (5) and Eq. (1) are,

$$\tan \varphi_{13} = R/P \quad \text{and} \quad -P/R . \quad (6)$$

As in the case of φ_{12}, φ_{13} is also fixed by finding the F_{steep} critical point nearest to the angle maximising F_k.

For φ_{23},

$$D_{kk} = R^2 \Lambda_2 \Lambda_3 + (P S_{\varphi_{23}} + Q C_{\varphi_{23}})^2 \Lambda_3 \Lambda_1 + (P C_{\varphi_{23}} - Q S_{\varphi_{23}})^2 \Lambda_1 \Lambda_2 \quad (7)$$

and

$$\tan \varphi_{23} = P/Q \quad \text{and} \quad -Q/P . \quad (8)$$

Following the above procedure, φ_{23} is also determined.

Results and Discussion

The structural parameters and spectral data for NSCl and NSF used in the present calculations are the same as those reported by Muller et al. [9] and those of NSBr by Peake and Down [10]. For disulphur monoxide the data were taken from the work of Hopkins et al. [11] and for the formyl radical and hypohalites from that of Ogilvie [12].

For all the molecules the angle parameters are reported in Table 1. From a critical survey of Table 1, one can classify the systems into three different categories. The thiazyl halides and disulphur monoxide have considerable values for the three angle parameters. Even $\varphi_{12} = 3°12'$ for NSCl and $3°54'$ for NSBr introduce a small change in the force constants. All the three angle parameters, therefore, are necessarily to be fixed to get an accurate set of force constants in the case of these molecules.

Table 1. Angle parameters.

Molecule	φ_{12}	φ_{13}	φ_{23}
NSF	25°12′	161°18′	126°48′
NSCl	3°12′	169°48′	126°18′
NSBr	3°54′	172°18′	132°30′
SSO	8°36′	167°36′	126°48′
HCO	27°	180°	167°36′
HOF	16°6′	180°	179°54′
HOCl	14°6′	180°	179°54′
HOBr	12°42′	180°	179°54′
HOI	23°18′	180°	179°54′

The formyl radical falls in the second category wherein two angle parameters are enough to get a reasonable force field. The value 180° for φ_{13} introduces no change in the F elements.

The hypohalites come under the third category wherein the problem could be solved with a single angle parameter. The values 180° and 179°54′ for φ_{13} and φ_{23} respectively introduce practically no change in the force constant values. It is sufficient if φ_{12} alone is fixed for such systems.

There is a clear low frequency separation in hypohalites. Hence the low frequency separation method can be applied to these molecules to get a reasonable force field. The approximation of low frequency separation is identified here with the angle parameters. In such cases, in general, the three dimensional problem can be solved with one angle parameter. The work on XY_3Z_2 [8] type molecules stands as a support to this view. Also when the centre atom is heavy when compared to the end atoms such an approximation holds good [6]. The possibility of solving a (3×3) order problem with a single angle parameter in the case of degenerate species has already been discussed by Ananthakrishnan [13].

Peacock et al. [14] have predicted some properties of the eigenvector matrix based on the fact that when two stretching (bending) modes occur in a (3×3) case, mostly the stretch-stretch (bend-bend) mixing is much more appreciable than the stretch-bend mixing. The L matrices obtained here are found to possess the properties predicted by Peacock et al.

The thiazyl halides, disulphur monoxide and the formyl radical are of "$\nu\nu\delta$" case for which L_{12}, L_{13} and L_{23} should be the smallest off-diagonal L elements. Since the coordinate numbering for these systems in the present calculations is YX stretch $= 1$, XYZ bend $= 2$ and YZ stretch $= 3$, the corresponding L elements are L_{13}, L_{12} and L_{32}. The L matrices of these systems conform fully with the predictions (Table 2).

The hypohalites are of "$\nu\delta\nu$" case. The present coordinate numbering is XYZ bend $= 1$, YX stretch

Table 2. Off-diagonal L matrix elements (in amu$^{-1/2}$).

Molecule	L_{12}	L_{13}	L_{21}	L_{23}	L_{31}	L_{32}
NSF	0.0022	0.0014	− 0.1219	0.0651	0.0456	0.0247
NSCl	0.0006	0.0019	− 0.1666	0.0478	0.0468	0.0377
NSBr	0.0002	0.0018	− 0.1826	0.0438	0.0528	0.0288
SSO	0.0034	0.0063	− 0.1455	0.0578	0.0532	0.0247
HCO	− 0.0216	0.0247	− 0.2024	0.0358	0.0530	0.0088
HOF	− 0.0462	0.0238	0.0018	− 0.0047	0.0782	− 0.0079
HOCl	− 0.0368	0.0222	0.0029	− 0.0022	0.0823	− 0.0138
HOBr	− 0.0331	0.0206	0.0030	− 0.0020	0.0845	− 0.0164
HOI	− 0.0312	0.0218	0.0028	− 0.0026	0.0889	− 0.0163

$=2$ and YZ stretch $=3$ and hence the smallest L elements are L_{21}, L_{23} and L_{31}. In the present work L_{32} is found to be smaller than L_{31} which may be attributed to the fact that in hypohalites there is considerable mixing between the YX stretching and the bending modes, the YZ stretching being pure. This is apparent from the angle parameters of these molecules. Such a deviation from the generally expected mixing has already been observed by Laane et al. [15] and Ramaswamy and Namasivayam [16] in their work on nitrosyl halides. It is found from the survey of the work of Karunanithi [17] that the smallest elements of the parametrised L matrices of nitrosyl halides are L_{21}, L_{23} and L_{32} instead of L_{21}, L_{23} and L_{31} for the same coordinate numbering as in the present work.

The force constants are reported in the usual order in Table 3. The comparison between the present values and the literature values is reasonably good. There is change of sign with the F_{13}

Table 3. Symmetry force constants (in mdynes/Å). P.S.: Present study.

Molecule	F_{11}	F_{22}	F_{33}	F_{12}	F_{13}	F_{23}	Ref.
NSF	10.851	2.932	0.401	0.358	0.079	0.072	P.S.
	10.910	3.000	0.400	0.460	0.140	0.140	[14]
	10.940	2.880	0.412	0.860	0.0	0.0	[9]
	10.709	2.871	0.411	0.095	− 0.044	0.019	[10]
NSCl	10.090	1.761	0.228	0.188	0.066	0.071	P.S.
	10.150	1.810	0.230	0.280	0.110	0.100	[14]
	10.040	1.490	0.265	0.040	0.0	− 0.014	[9]
	10.095	1.380	0.272	0.105	0.006	− 0.037	[10]
NSBr	9.924	1.760	0.166	0.221	0.062	− 0.082	P.S.
	9.875	1.294	0.220	0.010	0.076	− 0.032	[10]
SSO	8.473	4.425	0.505	0.560	0.126	0.143	P.S.
	8.249	4.430	0.512	0.151	− 0.009	0.128	[11]
	8.586	4.533	0.493	0.792	0.230	0.210	[20]
HCO	3.405	14.292	0.538	0.553	0.093	0.210	P.S.
	3.470	14.190	0.564	0.540	—	—	[21]
	3.102	14.359	0.705	0.271	− 0.596	0.301	[12]
HOF	7.153	4.175	0.654	0.002	0.009	0.134	P.S.
	7.205	4.327	0.671	—	0.103	0.346	[12]
	6.811	4.370	0.692	—	—	0.403	[22]
HOCl	7.276	3.542	0.472	− 0.018	0.011	0.095	P.S.
	7.350	3.860	0.475	—	—	0.266	[23]
	7.317	3.620	0.485	—	− 0.104	0.227	[12]
HOBr	7.198	3.237	0.379	− 0.025	0.006	0.078	P.S.
	7.143	3.594	0.395	—	—	0.343	[23]
	7.240	3.354	0.394	− 0.010	0.105	0.215	[12]
HOI	6.521	2.886	0.375	− 0.021	0.002	0.126	P.S.
	6.542	2.991	0.389	− 0.300	0.101	0.181	[12]

Table 4. Mean amplitudes of vibration (in Å). P.S.: Present study.

Molecule	σ_{X-Y}	σ_{Y-Z}	$\sigma_{X\ldots Z}$	Ref.
NSF	0.0355	0.0490	0.0780	P.S.
	0.0355	0.0489	0.0708	[14]
NSCl	0.0362	0.0560	0.0900	P.S.
	0.0362	0.0557	0.0838	[14]
	0.0378 ±0.0029	0.0526 ±0.0030	0.0766 ±0.0121	[24]
NSBr	0.0363	0.0546	0.0973	P.S.
SSO	0.0408	0.0371	0.0682	P.S.
	0.0408	0.0371	0.0615	[20]
HCO	0.0854	0.0362	0.1276	P.S.
	0.0754	0.0361	—	[25]
HOF	0.0704	0.0470	0.1012	P.S.
	0.0714	0.0374	0.1565	[26]
HOCl	0.0701	0.0469	0.1053	P.S.
	0.0692	0.0418	0.1027	[27]
HOBr	0.0703	0.0465	0.1079	P.S.
HOI	0.0721	0.0476	0.1058	P.S.

elements of SSO, HCO and HOCl. Such a discrepancy has been come across by Redington and Aljibury [4] also in the case of ONCl and ONBr.

Mean amplitudes of vibration of both the bonded and non-bonded atom pairs have been calculated and reported in Table 4 and these values compare well with the reported values.

The Coriolis coupling constants and inertia defects calculated here are given in Table 5 along with the available literature values. The comparison is fairly good. The ζ-sum rule, $\zeta_{12}^2+\zeta_{13}^2+\zeta_{23}^2=1$, is perfectly obeyed in all cases.

Table 5. Coriolis coupling constants and inertia defects (in amu Å^2). P.S.: Present study.

Molecule	$\lvert\xi_{12}\rvert$	$\lvert\xi_{13}\rvert$	$\lvert\xi_{23}\rvert$	Δ_0	Ref.
NSF	0.3595	0.7598	0.5417	0.1933	P.S.
				0.1897	[28]
NSCl	0.4489	0.8068	0.3841	0.2652	P.S.
	0.6283	0.6815	0.3752	0.2400	[29, 9]
NSBr	0.4882	0.8148	0.3124	0.2886	P.S.
SSO	0.4316	0.7929	0.4300	0.1821	P.S.
				0.1840	[18]
HCO	0.1886	0.9351	0.2997	0.0699	P.S.
HOF	0.0087	0.9777	0.2094	0.0567	P.S.
HOCl	0.0100	0.9875	0.1572	0.0605	P.S.
HOBr	0.0097	0.9916	0.1283	0.0636	P.S.
HOI	0.0108	0.9931	0.1251	0.0629	P.S.

Centrifugal distortion constants have also been calculated and compared with the previously reported values wherever available (Table 6). The agreement is fairly good except for τ_{xxxx}'s of NSCl and SSO which are less than the respective observed values. It has been pointed out by Ramaswamy et al. [18] that the calculated τ_{xxxx} of SSO for the angle variation in the range 0° to 180° is always less than the observed value. For HCO, only D_J (0.049 ± 0.019 MHz) [19] is available for comparison. The D_J for HCO obtained here is 0.0371 MHz which is well within the error limits.

Table 6. Centrifugal distortion constants (in MHz). P.S.: Present study.

Molecule	$-\tau_{xxxx}$	$-\tau_{yyyy}$	$-\tau_{zzzz}$	τ_{xxyy}	$-\tau_{xyxy}$	Ref.
NSF	8.9347	0.0542	0.0183	0.4246	0.0833	P.S.
	8.8343 ± 0.0158	0.0564 ± 0.0005	—	0.4479 ± 0.0034	0.0895 ± 0.0014	[28]
	8.8970	0.0570	—	0.4550	0.0900	[9]
NSCl	4.1587	0.0122	0.0061	0.0991	0.0366	P.S.
	6.9390	0.0130	—	0.1700	0.0360	[9]
NSBr	3.6412	0.0045	0.0028	0.0492	0.0221	P.S.
SSO	3.3117	0.0104	0.0045	0.1030	0.0240	P.S.
	4.6690	0.0103	0.0048	—	0.0300	[30]
HCO	16.1207	0.2099	0.0979	0.3304	0.6415	P.S.
HOF	5.6300	0.6436	0.3306	− 1.5060	1.6743	P.S.
HOCl	3.5353	0.1678	0.1082	− 0.6579	0.6972	P.S.
HOBr	2.1910	0.0644	0.0456	− 0.3344	0.3472	P.S.
HOI	1.4125	0.0346	0.0253	− 0.2024	0.2079	P.S.

Conclusion

The F_{steep} critical point procedure of Redington to determine the angle parameters can effectively be applied to bent XYZ type systems.

The multiplicity of solutions, that occurs in the other parametric procedures [1], is eliminated by the maximisation of the restoring force corresponding to the highest frequency, in Redington's method.

The L matrices obtained here are consistent with the predictions of Peacock et al. and the deviation in "$\nu\delta\nu$" case is accounted for.

The calculated molecular constants are found to compare well with the reference values and hence in conclusion it may be pointed out that the method of Redington and Aljibury, when applied to XYZ C_s point group systems, is as accurate as other conventional methods.

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