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FORCE FIELD STUDY OF SOME XZY_4-TYPE MOLECULES USING REDINGTON'S VIRIAL THEOREM APPROACH

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Force fields of $WOCl_4$, WOF_4 and $XeOF_4$ molecules belonging to the C_{4v} point group were computed using Redington's method. The angle parameters ϕ_{12}, ϕ_{13} and ϕ_{23} were fixed through "F_{steep} critical point" solutions under identical potential energy conditions. The Coriolis coupling constants, rotational distortion constants and mean amplitudes of vibration were also calculated and compared with literature values.

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1. *Introduction*

DeWames and Wolfram [1, 2] incorporated the isotopic shift in the secular equation using Green's function method and arrived at the force constants. Parametric representations [3–6] were used by many authors to arrive at a unique force field using additionally observed data such as Coriolis coupling constants, rotational distortion constants, etc. Redington and Aljibury [7] proposed a method to find the unique force field by using only the experimentally observed vibrational frequencies. This method has already been applied to (3×3) order problems [8–13]. In the present paper an attempt was made to investigate exclusively the applicability of Redington's method to $WOCl_4$, WOF_4 and $XeOF_4$ of XZY_4 type molecules belonging to the C_{4v} point group in order to fix a unique force field.

2. *Theoretical consideration*

The well known secular equation connecting molecular vibrational problems is the transformation matrix, L, which is connected with the internal symmetry coordinates, S, and the normal coordinate, Q

$$S = LQ, \tag{1}$$

$$L\tilde{L} = G, \tag{2}$$

$$\text{and} \quad F = \tilde{L}^{-1}\Lambda L^{-1}, \tag{3}$$

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where G is the inverse kinetic energy matrix, F is the symmetric force constant matrix and Λ equals the diagonal matrix constructed from the observed vibrational frequencies. In the parametric method the L matrix is evaluated by using the relation

$$L = L_0 C, \tag{4}$$

where L_0 is obtained purely from the G matrix and C is chosen either as a numerical parameter matrix [14] or an angle parameter matrix [15]. In Redington's approach C is for

$$\begin{bmatrix} C_\phi & S_\phi \\ -S_\phi & C_\phi \end{bmatrix} \quad \text{for} \quad 2\times 2 \quad \text{cases,}$$

$$\text{and} \quad C_{12} = \begin{bmatrix} C_{\phi_{12}} & S_{\phi_{12}} & 0 \\ -S_{\phi_{12}} & C_{\phi_{12}} & 0 \\ 0 & 0 & 1 \end{bmatrix}; \quad C_{13} = \begin{bmatrix} C_{\phi_{13}} & 0 & S_{\phi_{13}} \\ 0 & 1 & 0 \\ -S_{\phi_{13}} & 0 & C_{\phi_{13}} \end{bmatrix}$$

$$\text{and} \quad C_{23} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & C_{\phi_{23}} & S_{\phi_{23}} \\ 0 & -S_{\phi_{23}} & C_{\phi_{23}} \end{bmatrix} \quad \text{for} \quad 3\times 3 \quad \text{cases,}$$

where $C_\phi = \cos\phi$ and $S_\phi = \sin\phi$. The evaluation of the C matrix is based on the following assumptions:

1) The coordinate associated with the highest frequency is displaced and the rest of the coordinates are allowed to relax to arrive at a restoring force balance and minimum potential energy.

2) The restoring force associated with the highest frequency is maximized.

3) Each coordinate is considered having an identical potential energy.

The parametrized F matrix is calculated through the equation

$$F_k = \frac{|F|}{D_{kk}}, \tag{5}$$

where D_{kk} are the cofactors of the diagonal force constants and $|F|$ is the determinant value of the symmetrized force constant matrix F. Following Redington, it is found that:

$$F_{\text{steep}} = \sum_k^n T_k D_{kk}^{-1/2} \tag{6}$$

can be used to arrive at a unique force field. Here T_k are the constants depending on the geometry of the molecule and they can be obtained from the virial theorem.

Coriolis coupling constants [16], mean amplitudes of vibration [17, 18] and rotation distortion constants [19–22] are evaluated by the usual procedures.

3. *Results and discussion*

The structural parameters and spectral data for $WOCl_4$ are taken from Cyvin, Brockner and Havdau [23]; WOF_4 data from Robiette, K. Hedberg and L. Hedberg [24] and Alexander et al. [25] and the data for $XeOF_4$ are from Peka Tsao, Coer and Classeu [26]. The symmetry coordinates are essentially the same as those reported by Ramaswamy and Muthusubramanian [27]. The inverse kinetic energy matrix G is constructed by using Wilson's [28] S_{kt} vectors and it is essentially the same as reported by Saadmahmodi and Edger Wandling [29].

In the present work, to find the C matrix, ϕ_{12} is taken as the arbitrary parameter. The "F_{steep} critical point" function is displayed for all the ϕ_{12} values in the range of $-90°$ to $+90°$. The highest frequency is maximized for a value of ϕ_{12}. At this value the restoring force, F_1, associated with the bond having the highest frequency, is taken to be the maximum and the other restoring forces, F_2 and F_3 (restoring forces of the bonds are taken in the descending order of frequency assignments) are such that the whole molecular system is having a minimum potential energy. Thus, the balance of restoring forces F_1, F_2 and F_3 through F_{steep} at ϕ_{12} is achieved. The angles, ϕ_{13} and ϕ_{23} are fixed using the L_0 matrix constrained by ϕ_{12}. The C matrix is found using $C = \pi C_{ij}$. In order to isolate the genuine solution from the spurious solution, the C matrix which reproduces the observed rotation distortion constant D_J for $XeOF_4$ and the mean amplitude of vibration for WOF_4 and $WOCl_4$ is taken. The ϕ_{ij} parameters (ϕ_{12}, ϕ_{13} and ϕ_{23}) are 3°, $-2°18'$ and $-1°18'$ (*a* species) and $39°6'$, $-2°42'$ and $-4°24'$ (*e* species) for $WOCl_4$; 11°, $-12'$ and $-2°$ (*a* species) and $46°6'$, 0 and 0 (*e* species) for WOF_4 and $-1°18'$, 5° and 1° (*a* species) and $31°54'$, $-54'$ and 1° (*e* species) for $XeOF_4$. In the case of WOF_4, for *e* species, the maximization of highest frequency is achieved at $\phi_{12} = 46°6'$ which corresponds to F_{steep} maximum. The possibility of solving 3×3 order problems with a single angle parameter for degenerate species has already been discussed by Ananthakrishnan [30]. In all cases the coordinates are numbered in the order of descending eigen values of the G matrix.

The valence force constants are calculated and given in Table I. For $WOCl_4$, W—Cl stretching force constant $f_r = 2.1957$ md/Å, W—O stretching force constant $f_R = 9.2169$ md/Å, interaction force constants $f_{rr} = 0.2663$ md/Å and $f'_{rr} = 0.5131$ md/Å are in very good agreement with 2.19 md/Å, 9.14 md/Å, 0.27 md/Å and 0.55 md/Å respectively, as reported by Cyvin, Brockner and Havdau [23]. Similarly in the case of $XeOF_4$, $f_r = 3.2196$ md/Å, $f_R = 6.5792$ md/Å, f_α = (F—Xe—F bending) = 0.1150 md/Å and f_β(F—Xe = O bending) = 0.5659 md/Å are in good agreement with 3.26 md/Å, 7.08 md/Å, 0.12 md/Å and 0.53 md/Å respectively as reported by Willett, LaBouville and Ferraro [31]. It is observed here that Xe—F and W—F bonds are only 1/2 as strong as the Xe=O and W = O bonds respectively, which is consistent with Rundle $3e$—$4e$ type bonding.

As the mass of the central atom increases the bond length decreases and bond angle α(F—X—F) also decreases while β(F—X = O) increases, the force constant increases, i.e., the bonds X—F and X = O become stronger. For $XeOF_4$, β is slightly greater than 90°. This indicates that "the repulsive effect of the Xe = O is slightly greater than that of the lone-pair electron" [32]. The above statement holds in the case of WOF_4.

The mean amplitudes of vibration are given in Table II. For $WOCl_4$, the mean amplitudes $\sigma_{X-Y} = 0.0458$ Å; $\sigma_{X-Z} = 0.0337$ Å; $\sigma_{Y \ldots Z} = 0.0948$ Å; $\sigma_{Y_1 \ldots Y_2(\text{short})} = 0.1051$ Å and $\sigma_{Y_1 \ldots Y_3(\text{long})} = 0.0786$ Å are in good agreement with 0.0497 Å, 0.0336 Å, 0.0910 Å, 0.1027 Å and 0.0734 Å respectively as reported by Cyvin, Brockner and Havdau [23]. For WOF_4, the corresponding mean amplitude values 0.0407 Å, 0.0343 Å, 0.0930 Å, 0.0984 Å

TABLE I

Valence force constants (md/Å)

	$WOCl_4$	WOF_4	$XeOF_4$
f_r	2.1957[a]	4.6744	3.2196
f_{rr}	0.2663	0.3475	0.0174
f_{rr}'	0.5131	0.4778	0.2757
$f_{r\alpha}$	0.0055	−0.1852	−0.0960
$f_{r\alpha}'$	−0.0056	0.1482	0.0941
f_{α}	0.1756	0.2649	0.1150
$f_{\alpha\alpha}$	−0.0549	−0.0364	−0.0310
$f_{\alpha\alpha}'$	−0.0128	−0.0853	−0.0499
f_{rR}	0.0500	0.1831	−0.0887
$f_{r\beta}$	0.0151	0.1607	0.0835
$f_{r\beta}'$	0.0001	0.0393	0.0149
$f_{r\beta}''$	−0.0149	0.0349	−0.0394
$f_{R\alpha}$	−0.0431	0.1188	0.0282
$f_{\alpha\beta}$	−0.0411	−0.0548	−0.0086
$f_{\alpha\beta}'$	−0.0266	−0.0562	−0.0167
f_R	9.2169	9.4458	6.5792
$f_{R\beta}$	0.1073	−0.2529	0.4741
f_{β}	0.2717	0.5846	0.5659
$f_{\beta\beta}$	−0.0803	−0.2129	0.0489
$f_{\beta\beta}'$	0.0644	0.3248	0.1871

[a] This number of significant figures is retained in all four Tables to secure internal consistency in calculation.

TABLE II

Mean amplitudes of vibration (Å) at a temperature of 298.16 K

	$WOCl_4$	WOF_4	$XeOF_4$
σ_{X-Y}	0.0458[a]	0.0407	0.0472
σ_{X-Z}	0.0337	0.0343	0.0385
$\sigma_{Y...Z}$	0.0948	0.0925	0.0838
$\sigma_{Y_1...Y_2(\mathrm{short})}$	0.1051	0.0984	0.1091
$\sigma_{Y_1...Y_3(\mathrm{long})}$	0.0786	0.0795	0.0617

[a] See footnote to Table I.

and 0.0795 Å are in very good agreement with the electron diffraction data 0.041 Å, 0.036 Å, 0.097 Å, 0.094 Å and 0.083 Å respectively as given by Robiette, K. Hedberg and L. Hedberg [24]. Similarly for $XeOF_4$, the corresponding values 0.0472 Å, 0.0385 Å, 0.0839 Å, 0.1091 Å and 0.0617 Å are in good agreement with the electron diffraction data 0.046 Å, 0.0362 Å, 0.0803 Å, 0.1203 Å and 0.0610 Å respectively as given by Hargittai et al. [33]. This agreement suggests the reliability of the force field calculations.

TABLE III

Coriolis coupling constants

	$WOCl_4$	WOF_4	$XeOF_4$
α_7	0.3785[a]	0.4730	0.4176
α_8	0.8460	0.7311	0.7337
α_9	−0.4194	−0.5148	−0.4424

[a] See footnote to Table I.

The Coriolis coupling constants are given in Table III. For $WOCl_4$, the values $\alpha_7 = 0.3785$, $\alpha_8 = 0.8460$ and $\alpha_9 = -0.4194$ are in reasonable agreement with 0.46, 0.80 and -0.45 respectively as given by Cyvin, Brockner and Havdau [23]. Experimental values are not available for these molecules. In all cases the Coriolis sum rule $\alpha_7+\alpha_8+\alpha_9 = \frac{I_Z}{2I_X}$ is found to hold, where I_X and I_Z are the moments of inertia about the X and Z axes respectively.

The rotation distortion constants are given in Table IV. For $XeOF_4$, the value of $D_J = 0.2677$ KHz is in agreement with the experimental value of 0.32 ± 0.1 KHz given by Mortin and Wilson [34], D_J, D_{JK} and D_K are calculated for all the molecules and reported. A complete set of experimental values is not available.

TABLE IV

Rotation distortion constants (KHz)

	$WOCl_4$	WOF_4	$XeOF_4$
D_J	1.4436[a]	0.2273	0.2677
D_K	1.3750	−0.6147	−0.9913
D_{JK}	−2.7942	0.4953	0.8100

[a] See footnote to Table I.

The calculated molecular constants are found to agree well with the literature values and hence it is concluded that Redington's procedure can be successfully applied to molecules WOF_4, $WOCl_4$ and $XeOF_4$ having heavy central atoms.

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