The Force Field of Osmium Tetroxide

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The experimentally determined mean amplitude of vibration for the Os—O distance is used in addition to the four fundamental vibration frequencies to calculate force constants of the general valence force field for OsO_4. In addition, different potential models are applied to calculate sets of force constants based only on the frequencies. The comparison of the values obtained from the mean amplitude with those calculated with the use of Coriolis coupling coefficients shows: The experimental limit of error in the mean amplitude results in relatively large possible ranges for the force constants, especially for the interaction term F_{34} in species F_2. It seems that in general experimental mean amplitudes of vibration determined with the methods presently available are mostly not accurate enough to use for the calculation of precise interaction force constants.

Mean amplitudes of vibration are calculated for OsO_4 according to the L matrix method of Morino *et al.*, assuming different potential models. These values, together with those obtained from ζ constants, show that the resulting amplitude quantities are quite insensitive to the potential model used. The simple potential models lead to accurate values which are comparable to amplitudes obtained with a GVFF (general valence force field), using frequency data and Coriolis coupling constants.

In general it is not possible to calculate force constants of the general valence force field from frequency data alone. With additional experimental quantities as isotope shifts, Coriolis ζ constants, centrifugal distortion constants, mean amplitudes of vibration, and intensities of Raman lines the complete F matrix in symmetry coordinates can sometimes be calculated. There is the difficulty, however, that the possibilities of measuring these data with sufficient accuracy are limited.

Recently Seip and Stølevik [1] reported the results of an electron diffraction study on osmium tetroxide. The mean amplitudes of vibration, u_{Os-O} and $u_{O...O}$, were given by the authors. During our investigation of the problem described here, a set of OsO_4 force constants of a general valence force field was established using Coriolis coupling constants as additional observational data.[2] The ζ constants were obtained from infrared band contours.

In this paper we wish to give the results of a similar calculation using experimentally determined amplitudes of vibration as additional information. The force constants obtained are compared with those calculated by Levin and Abramowitz as well as with the results of calculations using a modified valence force field, the Urey-Bradley force field, and a general valence force field (approximation method [3]).

The fundamental vibrations of the OsO_4 molecule can be classified according to the irreducible representations (species) of the point group T_d:

$$\Gamma = A_1 + E + 2F_2$$

The vibration frequencies used in the present calculations are summarized in Table 1. The F matrix elements of $F_{11}(A_1)$ and $F_{22}(E)$ (with usual meaning [4]) can be calculated directly from $\nu_1(A_1)$ and $\nu_2(E)$. The submatrix of $F(F_2)$ may be obtained from $\nu_3(F_2)$, $\nu_4(F_2)$, and a mean amplitude of vibration. We used for this calculation the value $u_{Os-O} = 0.036 \pm 0.002$ Å given by Seip and Stølevik [1] for the mean amplitude of vibration of the Os—O distance. For the calculation of the possible range of the force constants only the values 0.0348 Å $< u_{Os-O} < 0.038$ Å were used, because values lower than 0.0348 Å result in complex solutions for L_{34}. The amplitude $u_{O...O}$ was not used in our calculations because of its relatively large error; cf. Table 5.[a]

According to the L matrix method of Morino et al.[5] the following equations are valid.

$$u^2_{Os-O} = \tfrac{1}{4}\, G_{11}\varDelta_1 + \tfrac{3}{4}\, L_{33}{}^2\varDelta_3 + \tfrac{3}{4}\, L_{34}{}^2\varDelta_4 \tag{1}$$

$$u^2_{O...O} = \tfrac{2}{3}\, G_{11}\varDelta_1 + \tfrac{1}{3}\, G_{22}\varDelta_2 + \tfrac{1}{6}(2L_{33} + L_{43})^2\varDelta_3 + \tfrac{1}{6}(2L_{34} + L_{44})^2\varDelta_4 \tag{2}$$

with

$$\varDelta_i = (h/8\pi^2\nu_i)\mathrm{coth}(h\nu_i/2kT) \tag{3}$$

Using the further equations [6]

$$\mathbf{F}^{-1} = \mathbf{L}\,\varLambda^{-1}\,\mathbf{L}', \qquad \mathbf{G} = \mathbf{L}\,\mathbf{L}' \tag{4}$$

it is possible to calculate the F matrix for the species F_2; in this case one applied eqn. (1) in addition to (4).

Table 1. Fundamental frequencies of OsO_4 (in cm^{-1}) from Levin and Abramowitz.[2]

$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
965	353	959.5	329

The resulting symmetry force constants for F_2 are listed in Table 2 as set II, and are compared with values calculated according to different methods. Sets of force constants calculated without use of additional experimental quantities besides vibration frequencies are given in Table 3.

A comparison of the values in Table 2 shows: The errors in the determination of the mean amplitudes of vibration result in possible ranges for the force constants which are especially large for F_{34}, although the sign of F_{34} is calculated correctly. It can be shown theoretically that $f_{d\alpha}-f_{d\alpha}'$ has to be greater than zero.[7] Generally it can be said that the mean amplitudes of vibration have to be determined with an accuracy of about $\pm 1\%$ to obtain F_{34} values with sufficiently small limits of error. Although the limits of error are much smaller for F_{33} and F_{44} (cf. set II in Table 2) than for the nondiagonal element they are still large compared to those of the corresponding elements in set I. On the other hand the possible range of F_{34} in set I encloses (contrary to set II) negative values for $f_{d\alpha}-f_{d\alpha}'$, which is theoretically impossible. F_{34} (set I) was obtained by Levin and Abramowitz[2] using both ζ_{33} and ζ_{44} (which are inconsistent in themselves) as parameters, taking F_{34} as a reasonable mean value between the two results. The fact that negative $f_{d\alpha}-f_{d\alpha}'$ values are possible within the limits of error is due to the influence of ζ_{33}.

A very good agreement is observed between the force constants calculated according to Fadini[3] (set III in Table 2) and those of set I and II. The quantities of set V show that in this case the MVFF is a good approximation, as is to be expected if there is a heavy central atom between small ligand atoms. The UBFF constants (set IV) are calculated to lie partly outside the ranges of

Table 2. Symmetry force constants in species F_2 calculated for OsO_4 according to different methods (in mdyne/Å).

		F_{33}	F_{44}	F_{34}
I	GVFF (using ζ values)	7.80 ± 0.05	0.425 ± 0.005	0.05 ± 0.10
II	GVFF (using u values)	7.21 ± 0.51	0.55 ± 0.12	$0.67 \begin{smallmatrix} +0.43 \\ -0.60 \end{smallmatrix}$
III	GVFF (approximation)	7.78	0.43	(0.01)
IV	UBFF	7.86	0.43	0.20
V	MVFF	7.79	0.43	0 (assumed)

Table 3. MVFF and UBFF force constants for OsO_4 (in mdyne/Å).

	MVFF		UBFF
f_d	8.03	K	7.47
f_{dd}	0.25	F	0.33
f_α	0.43	H	0.27
$f_{\alpha\alpha}$	0.02	F'	-0.03

values possible according to set I and II. It has been shown [8] that the simple Urey-Bradley force field used here cannot predict the GVFF of XY_4 type species with T_d symmetry.

The direct relations between Coriolis coupling coefficients and the elements of the symmetrised mean square amplitude matrix [9] Σ permit a calculation of the whole $\Sigma(F_2)$ submatrix, and of mean amplitudes of vibration from vibration frequencies and ζ values.[10] The Σ matrix for species F_2 may be obtained from [9]

$$\Sigma = L \, \Delta \, L' \tag{5}$$

using the relation [11]

$$\zeta^\alpha = L^{-1} \, C^\alpha \, (L^{-1})' \tag{6}$$

for the calculation of the L matrix. The resulting Σ matrix for OsO_4 is listed in Table 4, the elements $\Sigma_{11}(A_1)$ and $\Sigma_{22}(E)$ having been calculated directly from the frequencies. Two additional sets of Σ elements resulting from eqn. (5) with the assumption of different force fields are also summarized in Table 4. A comparison of the different sets of Σ matrix elements shows that the assumption of simplifying potential models is almost without effect on the diagonal elements, but that the percentage variation of the Σ_{34} values is large. The elements of set I (Table 2) which have been calculated using additional experimental quantities (here $\zeta_{33} = 0.14$ and $\zeta_{44} = 0.42$) have to be considered to be more reliable than the others.

From the Σ matrix the mean amplitudes of vibration are computed according to

$$u^2{}_{Os-O} = \tfrac{1}{4}(\Sigma_{11} + 3\Sigma_{33}) \tag{7}$$

$$u^2{}_{O\cdots O} = \tfrac{1}{3}(2\Sigma_{11} + \tfrac{1}{3}\Sigma_{22} + 2\Sigma_{33} + \tfrac{1}{2}\Sigma_{44} + 2\Sigma_{34}) \tag{8}$$

In Table 5 the u values for OsO_4 are compared with those resulting from electron diffraction measurements and those calculated, assuming different potential models. The table shows that the kind of potential has almost no effect on the u_{Os-O} values and that its influence on $u_{O\cdots O}$ is only small.

The Σ elements obtained from vibration frequencies and Coriolis coupling constants can be used to calculate the shrinkage effect for OsO_4 with a relatively high accuracy;[12,13]

$$\delta = (6^{1/2}/12R)(\tfrac{1}{6}\Sigma_{22} - \Sigma_{33} + \tfrac{5}{4}\Sigma_{44} - \Sigma_{34}) \tag{9}$$

Table 4. Mean-square amplitude matrix for OsO_4 according to different potential models. The elements are given in $Å^2$ at $298°K$.

		$\Sigma_{11}(A_1)$	$\Sigma_{22}(E)$	$\Sigma_{33}(F_2)$	$\Sigma_{34}(F_2)$	$\Sigma_{44}(F_2)$
I	GVFF (using ζ values)	0.001113	0.012940	0.001244	-0.000205	0.011679
II	UBFF	0.001113	0.012940	0.001248	-0.000401	0.011756
III	MVFF	0.001113	0.012940	0.001247	-0.000140	0.011654

Table 5. Mean amplitudes of vibration for OsO_4 obtained by different methods (in Å at 298°K).

		u_{Os-O}	$u_{O \cdots O}$
Electron diffraction [1]		0.036 ± 0.002	$(0.062-0.071)$ [a]
I	GVFF (using ζ values)	0.0348	0.0694
II	UBFF	0.0348	0.0687
III	MVFF	0.0348	0.0698

[a] No definite mean value for $u_{O \cdots O}$ and no definite limit of error was given in Ref. 1.

An incorrect relation for δ was used in one of the cited papers.[12] The experimentally determined Os−O bond distance used in the present calculations is $R = 1.711_6$ Å.[1] The value obtained for the shrinkage effect, *viz.*

$$\delta = 0.00188 \text{ Å}$$

seems to be more reliable than a previously calculated one ($\delta = 0.0020$ Å),[13] considering the more exact Σ matrix elements and the newly determined Os−O bond distance used here. The shrinkage effect determined from electron diffraction (0.002 Å)[1] is in agreement with both values.

Using eqn. (6) or the equation

$$\zeta_{33} = -\frac{\mu_O(F_{33} + F_{44} + 2F_{34})}{\lambda_3 - \lambda_4} + \frac{\lambda_3 + (1/2)\lambda_4}{\lambda_3 - \lambda_4} \qquad (10)$$

together with

$$\zeta_{33} + \zeta_{44} = \tfrac{1}{2}$$

the Coriolis coupling constants can be calculated for the different potential models. In Table 6 the obtained values are compared with the experimentally determined ones. Again the results show that the MVFF (with $F_{34} = 0$) represents a good approximation in the case of OsO_4. All calculated ζ constants agree quite well with the values obtained from IR band contours. Only the ζ_{33} value of the UBFF was found to lie far outside the limit of error of the experimental value.

Since the manuscript of this work was completed (at the University of Göttingen) some additional results of investigations on OsO_4 have appeared.

Table 6. Coriolis coupling constants for OsO_4 according to different methods.

		ζ_{33}	ζ_{44}
IR band contours [2]		0.14 ± 0.02	0.42 ± 0.04
I	GVFF (approximation)	0.125	0.375
II	UBFF	0.091	0.409
III	MVFF	0.126	0.374

Seip [15] has communicated as the final results of mean amplitudes of vibration from the series of electron-diffraction refinements:

$$u_{Os-O} = 0.036_0 \pm 0.0020 \text{ Å},$$
$$u_{O...O} = 0.070 \pm 0.0080 \text{ Å}.$$

The simultaneously published spectroscopic values of u for OsO_4 by Cyvin et al.[16] are based on UBFF and agree well with the slightly different sets of the various calculations of the present work. The calculated value [16] of ζ_{33} on the other hand shows a substantial deviation from the presently quoted experimental value.

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Mean Amplitudes of Vibration in Molecules with Internal Rotation: Halogenated Ethanes

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Mean amplitudes of vibration calculated from spectroscopic data are reported for hexafluoro-, hexachloro-, and hexabromo ethanes. The framework mean amplitudes of the same molecules are discussed, and calculated for various equilibrium configurations with differing angles of torsion. The resulting variations are found to be not at all negligible. For hexachloroethane taken as example the framework mean amplitudes of the long Cl···Cl distances vary from 0.1336 in the *cis* position to 0.1156 in *gauche*, and finally 0.0670 Å in the *trans* position; all values at 298°K. A general (approximate) formula is deduced for a variation of this kind, *viz.*

$$\langle \varDelta \varrho^2 \rangle_{\text{frame}} = (\alpha + \beta \, \cos\theta + \gamma \, \cos^2\theta)/\varrho^2$$

where α, β and γ are constants, θ is the equilibrium angle of torsion, and ϱ is the angle-dependent interatomic distance.

This is the first communication of our spectroscopic studies of molecules with internal rotation. The project has been initiated by the renewed interest of gas electron-diffraction investigations of such molecules, and highly inspired by the discussions at the first Symposium of Electron Diffraction at Oslo in February 1967. It is our purpose to supply some detailed data including mean amplitudes for framework vibrations, obtained from a spectroscopic normal-coordinate analysis of various molecules exhibiting internal rotation. As far as we know such material has been published before only for one molecule, *viz.* hexachlorodisilane, for which Morino and Hirota[1] have plotted the long Cl···Cl framework mean amplitude as a function of the torsional angle in different equilibrium positions. The framework mean amplitudes are of prime interest when interpreting the electron-diffraction measurements.[2,3] One has often resorted to assuming the framework mean amplitudes to be independent of the torsional angle, even in very recent works,[4] but also some empirical functional variations have been proposed.[5] In this connection it is felt that the spectroscopic data might be well appreciated. The following words from one of the cited papers [5] is taken as a direct challenge to us: