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Coriolis ζ Constants and Force Field for Osmium Tetraoxide

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Coriolis ζ constants for osmium tetraoxide were obtained from the infrared gas-phase band contours of the two triply degenerate vibrations. The interpretation of the ν_4 bending region is clarified through a consideration of the Coriolis coupling parameters. A normal coordinate analysis was performed using the ζ constants to define a unique force field for the F_2 symmetry species.

Introduction

Frequently, the correlation between vapor-phase infrared band contours and rotational constant functions permits either an estimate of molecular dimensions or an assignment of a particular vibration to its symmetry representation.[2] In addition, since band shapes are moderately sensitive functions of various dynamical parameters of the molecule, the characteristic contours of vibrationally degenerate modes are particularly useful in evaluating rotation–vibration interaction constants. Specifically, Edgell and Moynihan examined the dependence of P and R branch separations upon the Coriolis ζ constants of molecules whose rotational fine structures are not readily resolved.[3,4] Comparisons between the ζ values computed from band contours and from high-resolution analyses indicate that the approximate band shape method is reliable for molecules whose spectra are free from perturbations arising from hot-band transitions, Fermi resonances, or isotopic complications.[5-7]

The present study applies the contour method of evaluating Coriolis ζ constants to osmium tetraoxide. Since these coupling parameters impose constraints upon the numerous sets of force constants that are compatible with the observed vibrational frequencies, a unique potential energy expression is defined for this molecule.

Experimental Section

Spectra of the OsO_4, which was obtained commercially in sealed ampoules, were recorded with a Perkin-Elmer Model 521 spectrophotometer[8] at spectral slit widths of about 0.8 cm^{-1}. A conventional metal 5-cm CsI gas cell was used in the spectral determinations. Manipulations of the compound were made in an all-metal vacuum system. The ampoules containing the OsO_4 were broken either in the cell or in another portion of the vacuum system and subsequently transferred into the gas cell.

Infrared Band Contours and Coriolis Coupling Constants

The general features of the infrared and Raman spectra of OsO_4 have been previously reported by several authors.[9-11] Since the molecule belongs to the tetrahedral point group, the triply degenerate stretching and bending vibrations, ν_3 and ν_4, are infrared active and should exhibit a definite PQR band structure. For the ν_3 stretching vibration, the P, Q, and R branches are well defined, as shown in Figure 1; however, for ν_4 Hawkins and Sabol report the Q branch missing.[10] A representative scan for the ν_4 bending region is given in Figure 2. We do not assume a missing Q branch, but interpret the resulting spectrum as a merging of the Q and P branches as a consequence of the Coriolis interaction with the nearby ν_2 vibration. The band center is then taken at the maximum point of the leading edge of the Q branch at 329 cm^{-1}. The absorption band at approximately 353 cm^{-1} is identified as the ν_2 bending mode which is now made infrared active through the strong interaction between the ν_2 and ν_4 vibrations. This breakdown of the selection rules for ν_2 and concomitant degradation of the Q branch in ν_4, as a result of the Coriolis coupling between the two vibrations, are also observed, for example, in GeH_4, GeD_4, SnH_4, and SnD_4.[6,12] The infrared value for ν_2 correlates quite well with the Raman value of 335 cm^{-1} for the liquid.[9] Also, as we shall see below, the computed Coriolis coupling constants are consistent with this interpretation of the ν_4 region.

For the triply degenerate vibrational modes of spherical top molecules, Edgell and Moynihan demonstrated that the Coriolis interactions exhibit a first-order effect upon the separation of the P and R branch maxima.[3] This separation, $\Delta\nu_{P-R}$, is related to the Coriolis ζ_i by the expression

$$\Delta\nu_{P-R} = 4\left(\frac{BkT}{hc}\right)^{1/2}(1 - \zeta_i) \qquad (1)$$

The derivation assumes large moments of inertia, or a pressure-broadened contour for molecules with small inertial moments, and neglects the differences in the rotational constant B values for the ground and ex-

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[1] (a) National Institutes of Health; (b) National Bureau of Standards.

[2] (a) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933); (b) R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

[3] W. F. Edgell and T. E. Moynihan, *ibid.*, **27**, 155 (1957).

[4] W. F. Edgell and R. E. Moynihan, *ibid.*, **45**, 1205 (1966).

[5] A. Maki, E. K. Plyler, and R. Thibault, *ibid.*, **37**, 1899 (1962).

[6] I. W. Levin and H. Ziffer, *ibid.*, **43**, 4023 (1965).

[7] I. W. Levin and S. Abramowitz, *ibid.*, **43**, 4213 (1965).

[8] The identification of the commercial instrument in this paper does not imply recommendation or endorsement by the National Bureau of Standards or the National Institutes of Health.

[9] L. A. Woodward and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 615 (1956).

[10] N. J. Hawkins and W. W. Sabol, *J. Chem. Phys.*, **25**, 775 (1956).

[11] R. E. Dodd, *Trans. Faraday Soc.*, **55**, 1480 (1959).

[12] L. P. Lindeman and M. K. Wilson, *Z. Physik. Chem.* (Frankfurt), **9**, 29 (1956).

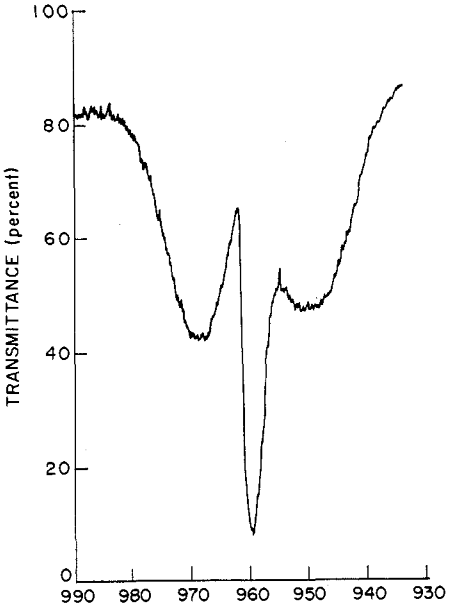

Figure 1.—Infrared gas-phase spectrum of OsO_4. The vibration-rotation band contour for the ν_3 fundamental vibration.

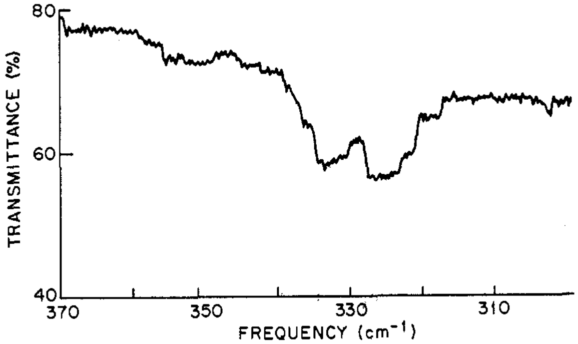

Figure 2.—Infrared gas-phase spectrum of OsO_4. The band contour for the ν_4 bending region.

cited states. The contours reported here were determined at T = 309.5°K. The quantities k, h, and c in eq 1 represent the fundamental constants.

For OsO_4, the P–R separation for the ν_3 mode, which is quite well behaved, was obtained by averaging six traces. The P–R separation for ν_4 was determined by doubling the measured R–Q separation. This approach is necessary since the Coriolis perturbation distorts the band such that a P branch maximum cannot be established. This R–Q separation was also an average of numerous expanded infrared scans of necessarily larger scale from that shown in Figure 2. The doubling of the R–Q distance has also been successfully applied to the normal and heavy germane and stannane species.[6,7] Using an Os–O bond distance of 1.717 A[13] to calculate a B value, eq 1 yields values of 0.14 and 0.42 for ζ_3 and ζ_4, respectively. This information is summarized in Table I, along with the observed frequency data. The primary source of error in the computed ζ constants arises from the errors in the P–R branch separations.

TABLE I

THE OBSERVED DATA FOR OSMIUM TETRAOXIDE

	Obsd freq, cm^{-1}	$\Delta\nu_{P-R}$[a]	ζ_i	$\Sigma\zeta_i$	Sum rule
ν_1	965[b]				
ν_2	353				
ν_3	959.5	18.5 ± 0.5	0.14 ± 0.02		
ν_4	329.0	12.5 ± 0.5[c]	0.42 ± 0.04		
				0.56	0.50

[a] Contours recorded at T = 309.5°K. [b] Reference 9. [c] $\Delta\nu_{P-R}$ obtained by doubling the R–Q separation.

However, by averaging many scans, the P–R distance can be determined within approximately 0.5 cm^{-1}. Also, although the bending modes have populated upper vibrational levels, the anharmonicities associated with hot-band transitions are probably small. Consequently, the distortions to the contour from this effect will also be small.

The consistency of these computed ζ constants is indicated by comparison with the theoretical ζ-sum rule for spherical top molecules; namely, that the $\Sigma\zeta_i = 0.50$. The calculated ζ constant sum of 0.56 compares favorably with the theoretical sum. Allowing that the measured ζ constants are not corrected for anharmonicities, the deviation from ideality for the ζ sum probably arises because of the uncertainties associated with the ν_4 contour. In addition, the small perturbation upon the contours from the osmium isotopes has been neglected.

It is, perhaps, instructive to illustrate the quantitative consistency obtained from band contours by assuming the theoretical ζ-sum rule of 0.50 and using the expression for $\Sigma\Delta\nu^i_{P-R}$ from eq 1 to calculate the rotational constant B. Since B is a function of the internuclear bond distance r_0, we can compare the actual bond distances of several spherical top molecules with those determined by contours. Although one would not wish to do any more than estimate bond lengths by this method, the calculated values agree very well with the measured bond distances, as shown in Table II. A propagation of error treatment suggests an uncertainty of approximately 0.13 A, while Table II indicates dispersions for r_0 within about one-half of this uncertainty. Consequently, we feel that the relatively good agreement of these calculated bond lengths adds further support to the quantitative use of band contour measurements for determining rotation–vibration interaction constants.

Potential Function

Various force constant studies have demonstrated the difficulty in determining unique intramolecular potential functions.[6,7,14] Consequently, additional molecular information must supplement the vibrational frequency data in order to limit the ambiguities inherent in the vibrational problem. The utility of Coriolis data in this regard is apparent when the dependence of the ζ constant is plotted as a function of the force field. Particularly, for OsO_4 the ambiguity

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(13) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962.

(14) J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964).

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL BOND LENGTHS

	r_{calcd}	r_{exptl}	$r_{\text{calcd}} - r_{\text{exptl}}$
CF_4[a]	1.27	1.317	−0.05
GeF_4[a]	1.72	1.67	+0.05
GeH_4[b]	1.58	1.527	+0.05
GeD_4[b]	1.53	1.527	0
SnH_4[c]	1.76	1.701	+0.06
SnD_4[c]	1.70	1.701	0
OsO_4[d]	1.78	1.717	+0.06

[a] Contour data from I. W. Levin and S. Abramowitz, *J. Chem. Phys.*, **44**, 2562 (1966). [b] Data from ref 7. [c] Data from ref 6. [d] Present work.

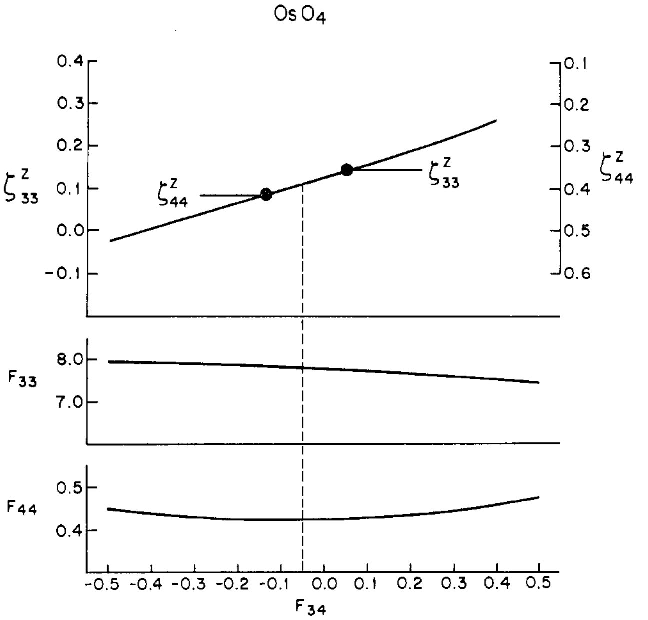

Figure 3.—Plots of F_{33}, F_{44}, ζ_{33}^z, and ζ_{44}^z as functions of F_{34} for the F_2 species of OsO_4.

arises in the triply degenerate species, where only two vibrational frequencies are available for determining the three symmetry force constants, F_{33}, F_{34}, and F_{44}. Figure 3 illustrates the dependence of ζ_3 and ζ_4 upon the elusive interaction force constant F_{34}. ζ is related to the force field through the eigenvector matrix **L** by

$$\zeta = \mathbf{L}^{-1}\mathbf{C}(\mathbf{L}^{-1})'$$

where $\mathbf{L}^{-1}$ represents the inverse of the eigenvector matrix. The matrix **C** is easily derived and is a function of only the atomic masses and molecular geometry.[15] The **L** matrix is obtained from a complete vibrational analysis that was cast in terms of the symmetry coordinates given in Table III.[6] The resulting plot suggests that many possible solutions of force constants exist that are compatible with the observed infrared frequencies.

TABLE III

SYMMETRY COORDINATES FOR OsO_4[a]

A_1 Species

$$S_1 = {}^1/_2(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

E Species

$$S_{2a} = r_0/2(\Delta\alpha_{14} - \Delta\alpha_{31} + \Delta\alpha_{23} - \Delta\alpha_{24})$$
$$S_{2b} = r_0/(12)^{1/2}(2\Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{14} - \Delta\alpha_{24} + 2\Delta\alpha_{34})$$

F_2 Species

$$S_{3a} = {}^1/_2(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$$
$$S_{4a} = r_0/\sqrt{2}(\Delta\alpha_{23} - \Delta\alpha_{14})$$
$$S_{3b} = {}^1/_2(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$
$$S_{4b} = r_0/\sqrt{2}(\Delta\alpha_{24} - \Delta\alpha_{13})$$
$$S_{3c} = {}^1/_2(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$
$$S_{4c} = r_0/\sqrt{2}(\Delta\alpha_{34} - \Delta\alpha_{12})$$

[a] The bending coordinates are scaled with r_0, the equilibrium bond distance. Δr_i and $\Delta\alpha_{ij}$ represent the internal bond-stretching and angle-displacement coordinates.

The potential function, however, can be limited if the ζ constants are known. The solid circles in Figure 3 represent the measured quantities, while the vertical dotted line indicates the final set of F_2 species force constants that represent the OsO_4 molecule. The uncertainties in the F_2 species force constants reflect the uncertainties in the ζ constant values. The relative flatness of the curves for F_{33} and F_{44} indicates that vibrational frequency data alone can determine reasonably well the principal force constants. However, we wish to emphasize that the curvature of the force constant plots depends upon the individual molecule under examination. Also, the actual form of a molecular vibration is often critically dependent upon the choice of the interaction force constant. The final set of symmetry force constants, which appear in Table IV, yield a value of 8.04 mdynes/A for the stretching force constant f_r, a reasonable value for the expected partial double-bond nature of the Os–O bond.

TABLE IV

FORCE CONSTANTS FOR OsO_4[a]

A_1 Species	
$F_{11} = f_r + 3f_{rr}$	8.77
E Species	
$F_{22} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$	0.39
F_2 Species	
$F_{33} = f_r - f_{rr}$	7.80 ± 0.05
$F_{34} = -\sqrt{2}(f_{r\alpha} - f_{r\alpha'})$	−0.05 ± 0.10
$F_{44} = f_\alpha - f_{\alpha\alpha'}$	0.425 ± 0.005

The Internal Valence Force Constants Are Defined by the **f** Matrix in Abbreviated Notation

f	$\Delta\alpha_{12}$	$\Delta\alpha_{34}$	$\Delta\alpha_{13}$	$\Delta\alpha_{23}$	$\Delta\alpha_{24}$	$\Delta\alpha_{14}$	Δr_1	Δr_2	Δr_3	Δr_4
$\Delta\alpha_{12}$	f_α	$f_{\alpha\alpha'}$	$f_{\alpha\alpha}$	$f_{\alpha\alpha}$	$f_{\alpha\alpha}$	$f_{\alpha\alpha}$	$f_{r\alpha}$	$f_{r\alpha}$	$f_{r\alpha'}$	$f_{r\alpha'}$
Δr_1							f_r	f_{rr}	f_{rr}	f_{rr}

[a] The units are expressed in millidynes per angstrom.

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[15] J. H. Meal and S. R. Polo, *J. Chem. Phys.*, **24**, 1126 (1956).