TABLE VI

SUMMARY OF THERMODYNAMIC FUNCTIONS

	$\Delta F_f°(25°)$, kcal mol^{-1}	$\Delta H_f°(25°)$, kcal mol^{-1}	$S°(25°)$, cal mol^{-1} deg^{-1}	$\bar{C}_p°\|_{25}^{100}$, cal mol^{-1} deg^{-1}
KHS(c)	...	−63.08	$(19 \pm 1)^a$	$(17 \pm 2)^a$
KHS(aq)	−64.58	−64.24	39.5	-13.8 ± 2
HS^-(aq)	2.88^b	-4.2^b	15.0^b	-48.8 ± 2
S^{2-}(aq)	21.7 ± 0.2	8.9 ± 0.4	-4.1 ± 2	-105 ± 9
H^+(aq)	0	0	0	31^c

[a] Estimated quantities. [b] Reference 16. [c] Reference 28.

Even though various values for the heats and free energies of formation of the aqueous sulfide ion have been reported from time to time, the adopted values for the entropy of the ion have remained rather constant. For example, during the last 30 years values ranging from −3.5 to −6.4 cal mol^{-1} deg^{-1} have been reported[9,16,29,30] and these are essentially reconfirmed by the results of this research. One of the objectives of the present work was to try to resolve the apparent discrepancy between the predicted[31] entropy of −20 cal mol^{-1} deg^{-1} for S^{2-}(aq) and the more positive experimentally determined values. The present research on the heat capacity of S^{2-}(aq) is in a similar situation, in that the predicted value[28] of $\bar{C}_p°|_{25}^{100} = -58$ cal mol^{-1} deg^{-1} is considerably different from our experimental value of $\bar{C}_p°|_{25}^{100} = -105$ cal mol^{-1} deg^{-1}. In fact, both the entropy and heat capacity function for S^{2-}(aq) closely resemble those for SO_4^{2-}(aq), which has entropy and $\bar{C}_p°|_{25}^{100}$ values of 4.8 and −108 cal mol^{-1} deg^{-1}, respectively. There is no evidence that aqueous sulfide and sulfate are structurally similar in water. However, the structurally sensitive thermodynamic functions do suggest that sulfide is either a more complex species in water than previously suspected or, alternatively, that its hydration sphere is not bound as tightly as predicted from other simple ions.

Temperature Dependence of pK_2^0 of H_2S(aq) to 250°. —Equation 18 which gives the variation of pK_2^0 as a function of temperature was derived by substituting

$$pK_2 = \frac{4500}{T} + 12.6 \log (T/298.15) - 1.29 \qquad (18)$$

the values of $\Delta F_d°(25°)$, $\Delta S_d°(25°)$, and $\Delta C_{pd}°|_{25}^{100}$ into the equation

$$\Delta F_d°(T) = \Delta F_d°(25°) - \Delta S_d°(25°)\Delta T + a(T)\Delta C_{pd}°|_{25}^{95}$$

recognizing that

$$\Delta F_d°(T) = 2.303RTpK_2^0 \qquad (19)$$

Because of the importance of H_2S in high-temperature aqueous processes, it is of interest to estimate K_2^0 for this species above 100°. For the dissociation of HSO_4^-(aq), $\Delta C_p°$ was reported not to change very rapidly above 90°. Assuming that $\Delta C_p°$ for the dissociation of HS^-(aq) behaves similarly, an extrapolation of pK_2^0, according to eq 18, can be made to 250°.

Comparison of the thermodynamic properties for the dissociation of HS^-(aq) and H_2O shows a remarkable similarity in the two weak acids. The value of pK_2^0 for H_2S(aq) is only 0.2 unit lower than pK_w^0 at 25°. This difference remains almost constant to 100° because of the nearly identical values of $\Delta S_d°(25°)$ for the dissociation reactions. Aqueous bisulfide does become slightly more acidic with increasing temperature than H_2O, as the values of $\Delta C_{pd}°|_{25}^{100}$ indicate. This means that significant concentrations of sulfide in solutions of moderate hydroxide concentration will be obtained only at temperatures much higher than 100°.

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The Vibrational Spectrum and Force Field of Osmium Tetroxide[1]

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Infrared spectra of the vapor and infrared and Raman spectra of CCl_4 solutions are reported for $Os^{16}O_4$ and $Os^{18}O_4$. Particular attention was given to measurement of the isotopic frequency shifts and the band contours, from which the Coriolis interaction constants are obtained. Anharmonicity corrections are estimated and the resulting harmonic frequencies are used to determine the general quadratic force constants of this molecule. The relative effectiveness of Coriolis constants and frequency shifts in determining the force field is compared. The valence stretching force constant, f_r = 8.32 mdyn/Å, supports the assumption of appreciable double-bond character for the Os–O bond. Standard-state thermodynamic functions for OsO_4 vapor are calculated for the temperature range 273–600°K.

Introduction

The vibrational spectrum and force constants of osmium tetroxide present a surprisingly vexing problem for such a simple molecule. OsO_4 has been shown to be tetrahedral (point group T_d) by electron diffraction of the vapor[2a] and by X-ray diffraction of the solid.[2b] The distribution of vibrational fundamentals for such

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) H. M. Seip and R. Stølevik, *Acta Chem. Scand.*, **20**, 385 (1966); (b) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, **19**, 157 (1965).

a molecule is well known to be $A_1 + E + 2\ F_2$; however, in this case the four fundamentals occur in two nearly coincident pairs, which has led to some confusion in the interpretation of the spectrum. Numerous investigations have been reported of the infrared spectra of the vapor,[3-6] CCl_4 solution,[4,6] and solid[6,7] and the Raman spectra of the vapor,[8] liquid,[7,9,10] CCl_4 solution,[6] aqueous solution,[9] and solid,[9-11] and the vibrational fundamentals are now known with some certainty to have the vapor-phase values 965 cm^{-1} (ν_1, A_1), 333 cm^{-1} (ν_2, E), 960 cm^{-1} (ν_3, F_2), and 329 cm^{-1} (ν_4, F_2).

The force constants of the A_1 and E fundamentals are obtainable directly from the vibrational frequencies, but the two F_2 fundamentals alone are not enough to determine the three force constants of that symmetry block. Appeal may be made to approximate force fields, and calculations have been reported for OsO_4 using Urey–Bradley,[8b,12] modified valence (F_{34} assumed zero),[12] orbital valence,[3,7] and other[13,14] force fields. It is, of course, much more satisfactory to obtain general quadratic valence force constants, and it has recently seemed that this had become possible for OsO_4 by supplementing the vibrational frequencies with Coriolis coefficients,[5,15] vibrational amplitudes obtained from electron diffraction,[16] and isotopic frequency shifts.[17] Unfortunately, the second of these methods is very insensitive and can only fix the force constants within large limits of error,[16] and the Coriolis coefficients for a molecule with as large a moment of inertia as this one must be determined from the infrared band contours, a method which for OsO_4 is complicated by the fact that the contours are perturbed in ways not yet fully understood.[6]

In the present work we have obtained the infrared and Raman spectra of $Os^{16}O_4$ and $Os^{18}O_4$, paying careful attention to measurements of band contours and isotope shifts. These results allow a comparison of the relative effectiveness of Coriolis constants and isotope shifts in determining the force field. We reach somewhat different conclusions than do Barraclough and Sinclair,[17] who have recently published a similar but less complete treatment.

Experimental Section

Preparation of $Os^{18}O_4$.—The $Os^{18}O_4$ was prepared by the reaction of $^{15}N^{18}O$ (98% ^{18}O enrichment) with powdered osmium metal (99.7% pure) at 800°. The osmium powder, in a quartz boat, was slowly heated in a quartz flow system through which passed a stream of enriched nitric oxide. The yellow-white osmium tetroxide was deposited beyond the heated zone in a bulb fused to the system and cooled by ice. After the reaction was completed and while the reactor was cooling, the nitric oxide was swept from the system with helium.

Raman Spectra.—Raman spectra of OsO_4 in CCl_4 solutions were obtained on a Cary Model 81 Raman spectrophotometer, using both mercury arc (4358-Å) and helium–neon gas laser (6328-Å) excitation. The instrument was calibrated with emission lines from a neon discharge tube. Concentrations varied from 0.3 to 4.0 g of OsO_4/ml of CCl_4; over this range, peak positions were not sensitive to concentration.

The frequencies are listed in Table I and the spectrum of the normal compound is shown in Figure 1. For $Os^{16}O_4$ the 10-cm^{-1} difference between the fundamentals ν_1 and ν_3 could be resolved because of their differing polarization, but in $Os^{18}O_4$ these two peaks are nearly coincident and only ν_1 could be obtained. Also in $Os^{18}O_4$, ν_2 could not be separated from the CCl_4 peak at 315 cm^{-1}. At the highest concentrations used, however, the fundamentals of OsO_4 were very much more intense than those of CCl_4; this and the agreement of the observed and calculated product ratios suggest that the underlying solvent band is not significantly affecting the measured position of ν_2.

TABLE I

RAMAN SPECTRA OF OsO_4 (CM^{-1})

	$Os^{16}O_4$		$Os^{18}O_4$
	Vapor[a]	CCl_4 soln[b]	CCl_4 soln[b]
$Os^{16}O^{18}O_3$, $\nu(Os{-}^{16}O)$ (A_1)			959 (8, pol)
ν_1	965.2	964.$_5$ (100, pol)	909.$_7$ (100, pol)
ν_3	960.1	954 (9)	
$Os^{16}O_3{}^{18}O$, $\nu(Os{-}^{18}O)$ (A_1)		908 (0.7, pol)	
$2\nu_2$		655 (0.9, pol)	
ν_2	333.1	335.$_2$ (45)	316.$_6$ (45)
ν_4	322.7		

[a] Reference 8b. A discrepancy between the infrared and Raman vapor frequencies of ν_4 is unexplained. [b] Frequencies are accurate to ±1 cm^{-1}. Approximate relative intensities for 6328-Å excitation are given in parentheses.

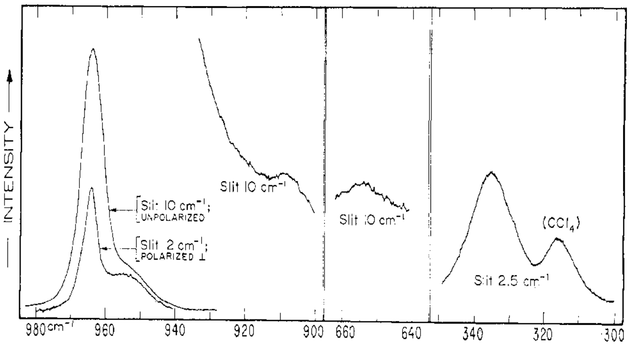

Figure 1.—Raman spectrum of a CCl_4 solution of normal OsO_4, concentration about 3 g/ml.

Infrared Spectra.—Infrared spectra were obtained using a Perkin-Elmer Model 521 spectrophotometer down to 250 cm^{-1} and a Beckman Model IR-11 for the region 400–140 cm^{-1}. Vapor bands were also examined under high resolution (about 0.4 cm^{-1}) with Perkin-Elmer Models 112G and E-13 double-pass grating spectrometers. All these instruments were calibrated with the IUPAC wave number tables[18] down to 590 cm^{-1} and with the rotational spectrum of water vapor[19] at longer wavelengths.

The vapor was examined in 1-m and 10-m folded-path gas cells;

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(4) R. E. Dodd, *Trans. Faraday Soc.*, **55**, 1480 (1959).

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(6) R. S. McDowell, *ibid.*, **6**, 1759 (1967).

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(18) IUPAC Commission on Molecular Structure and Spectroscopy, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, London, 1961.

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for some of the very weak bands, the cell and an attached trap containing solid OsO_4 were warmed with an infrared lamp to increase the vapor pressure to about 20 Torr. At the longer wavelengths, particular attention was paid to the elimination of the water vapor background, which can easily distort the contour of ν_4.

The same solutions used for the Raman spectra were also run in the infrared spectra, in 1-mm cells. Windows for both liquid and vapor were CsBr throughout most of the region and polyethylene for the far-infrared spectra.

The survey spectrum of normal OsO_4 vapor is shown in Figure 2; that of $Os^{18}O_4$ is essentially the same except for the expected frequency shifts. An illustration of the contour of ν_4 at higher resolution has been published previously.[6] Peak positions are given in Table II.

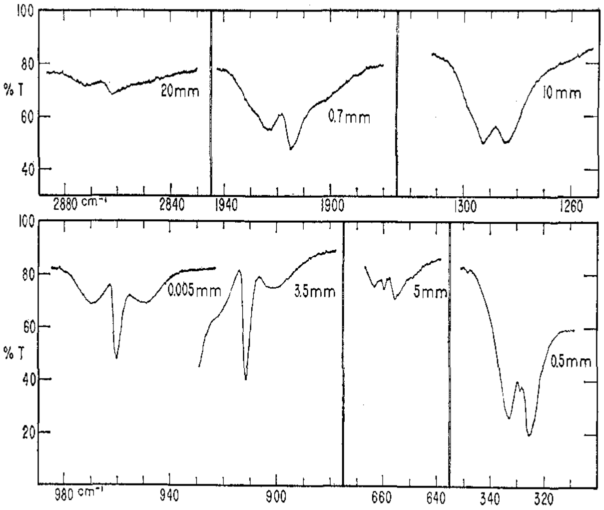

Figure 2.—Infrared survey spectrum of normal OsO_4 vapor in a 10-m cell. The approximate vapor pressures used are given for each trace.

TABLE II

INFRARED SPECTRA OF OsO_4[a]

Assignment	$Os^{16}O_4$ Vapor	$Os^{16}O_4$ CCl_4 soln	$Os^{18}O_4$ vapor
$3\nu_3$	R 2871 Q 2861.3 (0.2)	2846 (0.2)	R 2722 Q 2713.7
$Os^{16}O^{18}O_3$, 2ν (A_1)			R 1924 Q 1915.9 P 1904
$\nu_1 + \nu_3$		1917 sh (18)	
$2\nu_3$	R 1923 Q 1914.8 (22) P 1902	1905.8 (37)	R 1825 Q 1816.3 P 1805
$\nu_1 + \nu_4$, $\nu_2 + \nu_3$		~1290 sh	
$\nu_3 + \nu_4$	R 1292 P 1284 (1.6)	~1280 (1.8)	R 1227 P 1219
$Os^{16}O^{18}O_3$, ν (A_1)			R 971 Q 961.8 P 950
ν_3	R 968.9 Q 960.5 (3100) P 949.7	955.0 (2600)	R 920.3 Q 911.8 P 902.7
$Os^{16}O_3{}^{18}O$, ν (A_1)	R 920 Q 911.8 (6.7) P 901	907.8 (9.1)	
$2\nu_4$, $\nu_2 + \nu_4$	R 663 Q 659.4 (1.2) P 655	655.7 (1.6)	R 629 Q 625.8 P 621
ν_4	R 333.9 Q 329.0 (60) P 326.4	326.0 (280)	R 316.3 Q 312.7 P 308.8

[a] The approximate measured absorptivities, a, are given in parentheses. For solutions, a = (peak absorbance)/(path length (cm))(concentration (g/ml)). For the vapor, absorptivities were corrected to approximately the same units by taking $a = (6.7 \times 10^4)$(peak absorbance)/(path length (cm))(vapor pressure (Torr)).

At higher resolution, structure could be detected in the Q branch of ν_3, consisting of several lines separated by about 0.6 cm^{-1}. This is probably not splitting due to the osmium isotopes: the splitting is greater than expected,[20] the observed intensity distribution does not correlate well with the relative isotopic abundances of osmium, and there is no gap corresponding to the missing ^{191}Os isotope. It seems quite probable that hot bands are responsible for this structure. The reported Q-branch positions are for the strongest of these lines, and since the structure was the same for both $Os^{16}O_4$ and $Os^{18}O_4$, it is likely that the isotopic frequency shifts have been satisfactorily determined.

Results

Assignments and Harmonic Frequencies.—A discussion of the assignments of the fundamentals has been given in ref 6 and need not be repeated. Assignments of all observed infrared and Raman bands are given in Tables I and II.

Before proceeding to the calculation of the force constants, it is necessary to estimate the harmonic vibrational frequencies ω_i. For OsO_4 this is complicated by the fact that ν_1 and ν_3 are nearly coincident, as are ν_2 and ν_4; this results in a mixing of the overtone and combination bands to an extent that precludes obtaining the full set of ten anharmonicity constants X_{ij}. To obtain ω_1 and ω_2, we resort instead to a method of approximation due to Dennison.[21] We write

$$\omega_i \approx \nu_i(1 + \alpha_i), \qquad \omega_i^* \approx \nu_i^*(1 + \nu_i^*\alpha_i/\nu_i) \quad (1)$$

where the asterisk indicates the isotopic frequencies. Requiring the harmonic frequencies to satisfy the product rule—in this case, $\omega_i^*/\omega_i = (m_O/m_O^*)^{1/2} = 0.9427$—allows us to solve for α_i using the solution values of ν_i from Table I. These corrections were then applied to the vapor frequencies of Huston and Claassen.[8b] The results are given in Table III. The error in using this approximation is probably small, and the force constants obtained from the ω's will certainly be more accurate than those obtained using the ν's as has been done heretofore.

TABLE III

VAPOR-PHASE FUNDAMENTALS: OBSERVED AND ESTIMATED HARMONIC FREQUENCIES (CM^{-1})

	$Os^{16}O_4$		$Os^{18}O_4$	
i	ν_i	ω_i	ν_i	ω_i
1 (A_1)	965.2	974.3	...	918.5
2 (E)	333.1	345.2	...	325.4
3 (F_2)	960.5	976.9	911.8	926.6
4 (F_2)	329.0	345.0	312.7	328.3

We can approximate the value of ω_3 from the observed overtones and combinations as follows: from vapor frequencies, we estimate $X_{33} = -3.3$ cm^{-1}, $X_{34} = -1.5$ cm^{-1}; from solution frequencies, X_{13} =

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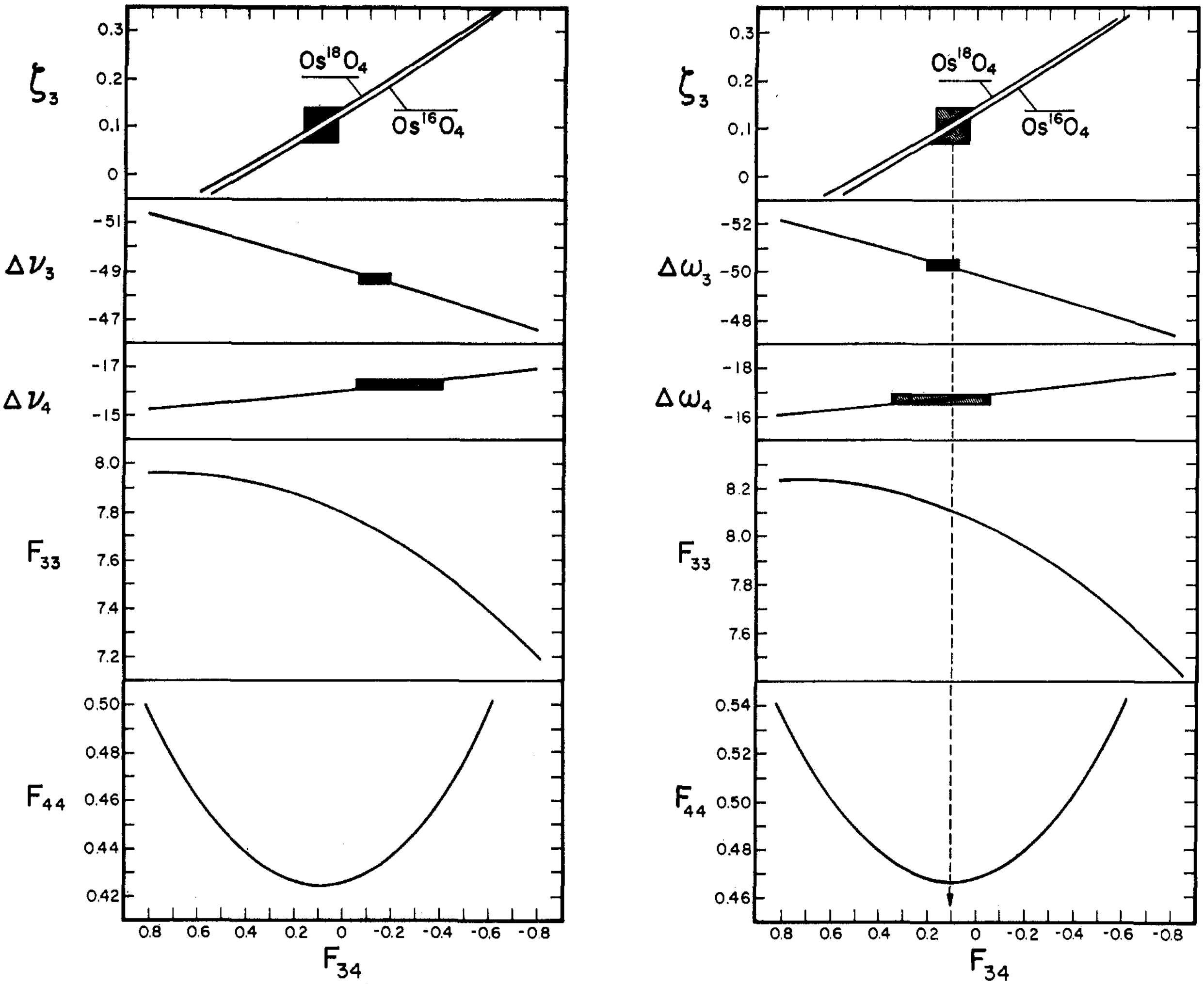
(20) The isotopic shift for ν_3 could amount to as much as 0.6 cm^{-1} for a 1-amu change in the osmium mass only in the unlikely circumstance that almost all of the isotopic effect was concentrated in ν_3, with ν_4 showing practically no shift. Actually, using the force constants of Table IV, the frequency shifts expected for a 1-amu change in the osmium mass are about 0.26 cm^{-1} for ν_3 and 0.14 cm^{-1} for ν_4. To account for a shift of 0.6 cm^{-1} for ν_3, the force constants would have to be $F_{33} = 4.84$, $F_{44} = 1.57$, and $F_{34} = -1.96$ mdyn/Å. Such a force field is hardly reasonable and would predict $\Delta\omega_3(^{16}O-^{18}O) = 42.6$ cm^{-1}, $\Delta\omega_4(^{16}O-^{18}O) = 19.4$ cm^{-1}, $\zeta_3 = 0.87$, and $\zeta_4 = -0.37$, all of which are drastically out of line with the observations.

(21) D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940).



(a) OBSERVED FREQUENCIES (b) HARMONIC FREQUENCIES

Figure 3.—Force constant displays for the triply degenerate species of OsO_4, using (a) observed frequencies and (b) estimated harmonic frequencies. The force constants have the units mdyn/Å. The shaded blocks represent observed values and their estimated errors, and the vertical dashed line in (b) shows the preferred solution.

-2.0 cm^{-1}, $X_{23} \approx 0$ cm^{-1}. The harmonic frequency is then[22]

$$\omega_3 = \nu_3 - 4X_{33} - {}^1/_2(X_{13} + 2X_{23} + 3X_{34}) = 976.9 \text{ cm}^{-1}$$

Now with the usual approximation for the anharmonicity constants of the isotopic molecule

$$X_{ij}^* = (\nu_i^*\nu_j^*/\nu_i\nu_j)X_{ij} \qquad (2)$$

we obtain $\omega_3^* = 926.6$ cm^{-1}.

At this point we encounter a problem. The product rule requires

$$\frac{\omega_3^*\omega_4^*}{\omega_3\omega_4} = \frac{m_O}{m_O^*}\left(\frac{M^*}{M}\right)^{1/2} = 0.9026$$

while for the observed frequencies $\nu_3^*\nu_4^*/\nu_3\nu_4 = 0.9023$. An observed product ratio which is less than the calculated value is somewhat unusual and implies that neither eq 2 nor Dennison's approximation, eq 1, is applicable. Presumably the anomaly could be in the anharmonicity constants involving ν_3 or ν_4 or both. However, as will be discussed shortly, there are reasons for believing that ν_4 is perturbed by interaction with the fundamental ν_2, and it is probable that this interaction could affect the anharmonicity constants. X_{34}, however, at least approximately obeys eq 1 (*cf.* the combination band $\nu_3 + \nu_4$), and so we will choose to accept the values of ω_3 and ω_3^* calculated above. *Faute de mieux,* we estimate ω_4 to be 345 cm^{-1}, and ω_4^* is then fixed by the product rule.

Band Contours and Coriolis Constants.—The separation of the P- and R-branch maxima in the infrared-active fundamental ν_i of a spherical-top molecule is

$$\Delta\nu_i = 3.335(1 - \zeta_i)(BT)^{1/2}$$

where ζ_i is the first-order Coriolis interaction constant. For an Os–O distance[1] of 1.7116 Å, the rotational constants are $B = 0.1349$ cm^{-1} for $Os^{16}O_4$ and 0.1199 cm^{-1} for $Os^{18}O_4$.

The Coriolis constants obtained in this way from the band contours are $\zeta_3 = 0.09$ and $\zeta_4 = 0.64$; they clearly violate the ζ-sum rule $\zeta_3 + \zeta_4 = {}^1/_2$. Supposedly[6] the reason for this is that the contour of ν_4

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[22] It should be noted that the method of correcting for anharmonicity used by Barraclough and Sinclair[17] is not correct.

TABLE IV

SYMMETRY AND VALENCE FORCE CONSTANTS OF OsO_4 (MDYN/Å)

$F_{11} = f_r + 3f_{rr}$	8.95 ± 0.09	f_r	8.32 ± 0.06
$F_{22} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$	0.374 ± 0.011	f_{rr}	0.21 ± 0.03
$F_{33} = f_r - f_{rr}$	8.11 ± 0.08	$f_\alpha - f_{\alpha\alpha}$	0.421 ± 0.009
$F_{44} = f_\alpha - f_{\alpha\alpha'}$	0.467 ± 0.013	$f_{\alpha\alpha} - f_{\alpha\alpha'}$	0.046 ± 0.009
$F_{34} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'})$	0.10 ± 0.10	$f_{r\alpha} - f_{r\alpha'}$	0.07 ± 0.07

is perturbed by second-order Coriolis interaction with the nearby fundamental ν_2; the unusual weakness of the Q branch of ν_4 confirms that there is something irregular about this band. On the other hand, second-order Coriolis interaction between ν_1 and ν_3 is forbidden, and ν_3 exhibits a normal contour. It seems reasonable, then, that the value of ζ_3 derived from band contour measurements will be useful in determining the force field, and several treatments have used this approach.[5,6,15-17]

TABLE V

COMPARISON OF SYMMETRY FORCE CONSTANTS

Constraining parameters	F_{11}	F_{22}	F_{33}	F_{44}	F_{34}	Ref
ζ_3, ζ_3^*, $\Delta\omega_3$	8.95 ± 0.09	0.37 ± 0.01	8.11 ± 0.08	0.47 ± 0.01	0.10 ± 0.10	This work
ζ_3, ζ_3^*, $\Delta\nu_3$	8.85 ± 0.32	0.37 ± 0.02	8.01 ± 0.08	0.454 ± 0.018	-0.012 ± 0.08	17
ζ_3, ζ_4	8.77	0.39	7.80 ± 0.05	0.425 ± 0.005	0.05 ± 0.10[a]	5
Mean ampls	...	...	7.21 ± 0.51	0.55 ± 0.12	$0.67\begin{cases}+0.43\\-0.60\end{cases}$	16

[a] Because of differences in choosing the signs of the symmetry coordinates, F_{34} as used in ref 5 and 6 is the negative of our F_{34}.

We find the ν_3 P-R branch separations to be 19.2 cm^{-1} for $Os^{16}O_4$ and 17.6 cm^{-1} for $Os^{18}O_4$ at 299°K, yielding Coriolis constants $\zeta_3 = 0.093$ and $\zeta_3^* = 0.119$. In each case we estimate an uncertainty of ± 0.5 cm^{-1} in the spacing, which corresponds to an estimated error of ± 0.025 in the ζ's.

Force Constant Calculations

The relations between the force constants, vibrational frequencies, and Coriolis constants for an XY_4 molecule are well known.[23] We have used the 1963 NAS-NRC recommended values of the physical constants and 190.2 amu for the atomic weight of osmium.

In Figure 3 we have plotted for the F_2 symmetry block the diagonal force constants, frequency shifts, and Coriolis constants as functions of the off-diagonal force constant.[24] In Figure 3(a) the force constant curves give solutions which reproduce the observed frequencies of $Os^{16}O_4$ (Table III); in Figure 3(b) the solutions reproduce the estimated harmonic frequencies. The shaded blocks indicate the values and estimated errors of the observed frequency shifts (assuming an uncertainty of ± 0.2 cm^{-1}) and the Coriolis constants. The solutions represented by these blocks should, of course, lie vertically above one another and thus define a preferred range of values for F_{34} and hence also values for the diagonal force constants. We note that if the observed frequencies are used, Figure 3(a), this is not so, and in fact even the sign of F_{34} is in doubt. With the harmonic frequencies, however, Figure 3(b), the frequency shifts and Coriolis constants both suggest a value of F_{34} of about 0.1 mdyn/Å. The following points are worth noting.

(1) The frequency shift of ν_4 is relatively useless in fixing F_{34}, since it gives a range of values about 3 times that obtained from the ν_3 shift for the same estimated error in $\Delta\nu$.

(2) The frequency shift of ν_3 and the Coriolis constant ζ_3 are equally good for defining the force field, *if the anharmonicity corrections are known.* The important point here is that the relation between the off-diagonal force constant and the Coriolis constant is almost unaffected by anharmonicity; thus if the anharmonicity cannot be estimated—and this will often be the case—the Coriolis constant will still determine a good value of F_{34}, while the frequency shift probably will not.

As discussed in the previous section, the anharmonicity corrections for the F_2 block are approximate only. It is difficult to estimate their probable errors; but while ± 0.2 cm^{-1} is a reasonable estimate for the uncertainty in the observed frequency shifts $\Delta\nu$, it is doubtless rather optimistic for the $\Delta\omega$. In choosing $F_{34} = 0.10 \pm 0.10$ mdyn/Å, therefore, we are influenced primarily by the Coriolis constants, which give quite consistent results for the two isotopes.

The diagonal force constants, of course, are quite sensitive to the anharmonicity corrections, and although our estimated harmonic frequencies may not be dependable for determining the off-diagonal force constant without the help of the Coriolis constant, they certainly provide more accurate diagonal force constants than would be obtained by neglecting anharmonicity.

Our final values for the harmonic force constants are given in Table IV. The errors quoted there for F_{11} and F_{22} reflect an estimated uncertainty of ± 5 cm^{-1} in ω_1 and ω_2; the error in F_{34} has been discussed above. For the diagonal force constants of the F_2 block, we have estimated the limits due to an uncertainty of ± 5 cm^{-1} in ω_3 and ω_4; these are considerably greater than the limits due to the estimated error in F_{34} and hence provide a more conservative estimate of the true reliability of these force constants.

Our force constants are compared in Table V with other sets of symmetry force constants which have been reported. Our diagonal constants are somewhat higher than those of other investigators because of our more complete corrections for anharmonicity. The relative unsuitability of mean amplitudes of vibration

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(23) For example, L. H. Jones and M. Goldblatt, *J. Mol. Spectry.*, **2**, 103 (1958).

(24) All force constants quoted in this paper have the units mdyn/Å ($= 10^2 N/m$). The symmetry force constants F_{11}, F_{22}, F_{33}, F_{34}, and F_{44} are sometimes written F_{11}, $\rho^2 F_{22}$, F_{33}, ρF_{34}, and $\rho^2 F_{44}$, where ρ is the reciprocal of the Os-O distance.

in determining the force field is apparent from the final set in Table V.

Discussion

The off-diagonal force constant F_{34} deserves special mention. Our value appears to agree with that of Levin and Abramowitz,[5] but their reported result is the mean of those determined from ζ_3 and ζ_4, which are mutually inconsistent.[6] Using ν_3 alone, they obtain $\zeta_3 = 0.14$, $F_{34} = -0.05$ mdyn/Å; our measurements, however, do not support so high a value of ζ_3. Barraclough and Sinclair[17] measured the contour of ν_3 for $Os^{18}O_4$ and obtained a result similar to ours (their $\zeta_3{}^* = 0.14$), but they used Levin and Abramowitz's results for $Os^{16}O_4$. They obtain a positive value of F_{34} (≈ 0.02 mdyn/Å) for the isotopic molecule, but their final result is negative because of Levin and Abramowitz's result for the normal molecule. We believe that most of the evidence supports a positive value for this force constant and feel that in reporting $F_{34} = 0.1 \pm 0.1$ we have spanned the probable range. It is perhaps worth mentioning that there are grounds[25] for expecting that $f_{r\alpha}$ is greater than $f_{r\alpha}'$, and hence that F_{34} is positive; this rule is based on an approximate method of solving the secular equation but seems to hold generally for XY_4 molecules.

The force constants determined here are of special interest for the question of extremal force fields. Attention has recently been focused on the suggestion[26-28] that for second-order secular equations of XY_n molecules which are weakly mass coupled (*i.e.*, $m_X \gg m_Y$), the force field will be closely approximated by the condition that the diagonal force constant primarily associated with the lower vibrational frequency be a minimum. Clearly this condition is almost exactly satisfied for OsO_4 (Figure 3(b)). For some classes of molecules the extremal force field approximation fails,[28,29] but its obvious suitability for OsO_4 suggests that it may be applicable also to RuO_4 and to tetrahedral oxo anions of the heavier elements.

The bonding in OsO_4 has been discussed by Woodward and Roberts.[7] Both the Os–O stretching force constant ($f_r = 8.32$ mdyn/Å) and the bond length indicate that the Os–O bonds have appreciable double-bond character.

Thermodynamic Functions.—Standard-state thermodynamic functions for OsO_4 vapor are given in Table VI. These were calculated in the rigid-rotator harmonic-oscillator approximation, using the observed fundamentals of Table III and $B = 0.1349$ cm^{-1}.

Table VI

Thermodynamic Functions of Osmium Tetroxide

Temp, °K	$C_p°/R$	$(H° - H_0°)/RT$	$-(F° - H_0°)/RT$	$S°/R$
273.15	8.56	5.98	28.62	34.60
298.15	8.91	6.21	29.15	35.36
300	8.93	6.23	29.19	35.42
313 (mp)	9.10	6.34	29.46	35.80
350	9.54	6.66	30.18	36.84
400	10.06	7.05	31.10	38.15
403 (bp)	10.08	7.07	31.15	38.23
450	10.48	7.41	31.95	39.36
500	10.83	7.74	32.75	40.48
550	11.12	8.03	33.50	41.53
600	11.36	8.30	34.21	42.51

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[28] D. E. Freeman, *ibid.*, **27**, 27 (1968).

[29] W. Sawodny, *ibid.*, **30**, 56 (1969).