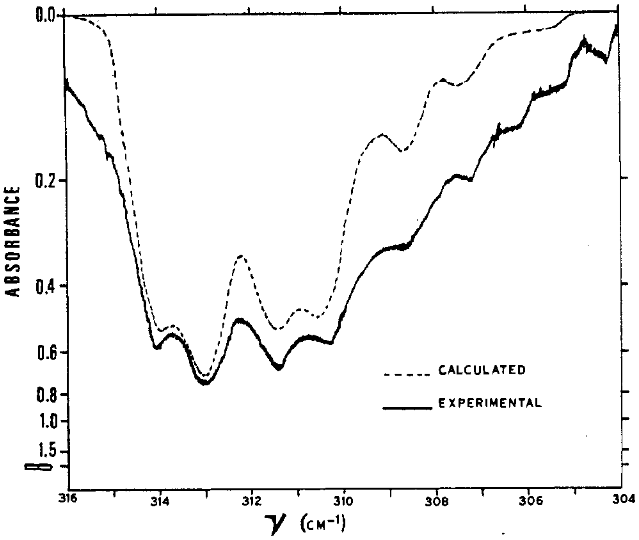

Figure 1.—Infrared spectrum of xenon dichloride.

constant, we have assumed that the entire band is due to the asymmetric stretching mode of a linear, symmetric $XeCl_2$ molecule and that the 314.1-cm^{-1} peak is predominantly due to the 35–129–35 species. Each line was assumed to have the same gaussian shape with a σ value equal to 0.37 cm^{-1}, selected parametrically to give the best reproduction of the experimental spectrum. The calculated frequencies are listed in Table I. The composite spectrum is shown in Figure 1 (dashed curve) and it compares quite well with the experimental spectrum (solid curve). The agreement shows that the spectrum can be confidently attributed to ν_3 of symmetric linear $XeCl_2$.

The absence of other absorptions attributable to the symmetric stretch is consistent with the deduced $D_{\infty h}$ symmetry. The bending mode, ν_2, would undoubtedly absorb below the limit of our spectral range, 200 cm^{-1}. The asymmetric stretching force constant, $k_r - k_{rr}$, is 1.317 mdynes/A, approximately half that of XeF_2 and KrF_2 (respectively, 2.60 and 2.59 mdynes/A).[4] The lower force constant of $XeCl_2$ reflects the expected weakness of the xenon–chlorine bond relative to the xenon–fluorine bond.

TABLE I

OBSERVED AND CALCULATED SPECTRUM OF XENON DICHLORIDE ($k_r - k_{rr}$ = 1.317 mdynes/A)

Species	Normalized abundance	Frequency, cm^{-1} Calcd	Obsd
35–128–35	0.071	314.53	
35–129–35	0.981	314.10	314.1
35–130–35	0.152	313.67	
35–131–35	0.788	313.25	
35–132–35	1.000	312.84	313.0
35–134–35	0.387	312.03	
35–128–37	0.046	312.0	
35–129–37	0.640	311.5	311.4
35–136–35	0.331	311.2	
35–130–37	0.099	311.1	
35–131–37	0.514	310.7	
35–132–37	0.653	310.3	310.4
35–134–37	0.252	309.4	
37–128–37	0.008	308.99	
35–136–37	0.216	308.6	
37–129–37	0.105	308.55	308.6
37–130–37	0.016	308.12	
37–131–37	0.084	307.69	
37–132–37	0.106	307.27	
37–134–37	0.041	306.44	
37–136–37	0.035	305.64	

Acknowledgment.—We gratefully acknowledge research support from the Office of Naval Research.

(4) J. J. Turner and G. C. Pimentel in "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 101.

Correspondence

Coriolis ζ Constants and Force Field for Osmium Tetroxide[1]

Sir:

The recent paper with this title by Levin and Abramowitz[2] is at variance with some conclusions reached in studies on the spectrum of OsO_4 in this laboratory. The infrared spectrum down to 140 cm^{-1} has been obtained here for the vapor (meter cell at pressures up to 10 mm, resolution about 0.5 cm^{-1}), CCl_4 solution (concentrations up to 1 g/ml in a 1-mm cell), and solid in both amorphous and crystalline (annealed) phases, deposited on a cold window at 80°K. In addition, polarized Raman spectra of CCl_4 solutions were obtained. This is the most extensive work on the vibrational spectrum of OsO_4 yet reported, and has led to the following conclusions.

(1) No trace of the band reported by Levin and Abramowitz[2] at 353 cm^{-1} and assigned by them to ν_2 (E) was found in vapor, solution, or solid spectra at concentrations sufficient to cause complete absorption in the ν_4 band. Their band lies in the center of a group of very strong water vapor lines and is apparently spurious. The true position of ν_2 is found in the Raman spectrum of solutions as a strong, depolarized band at 333 cm^{-1}, which does not coincide with the infrared solution band at 326 cm^{-1} (ν_4). That this 7-cm^{-1} difference is real was confirmed by the infrared spectrum of the crystalline solid, which shows a strong band at 320 cm^{-1} (ν_4) and a weaker band at 330 cm^{-1} which must be ν_2, activated in the solid (as is ν_1) by the C_2 site symmetry of the molecule.[3] Presumably its value in the vapor phase is about 335 cm^{-1}.

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) I. W. Levin and S. Abramowitz, *Inorg. Chem.*, **5**, 2024 (1966).

(3) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **19**, 157 (1965).

(2) Contrary to previous statements,[2,4] the ν_4 (F_2) band in the vapor phase does have the PQR structure expected for a tetrahedral molecule, and the Q branch (329.1 cm^{-1}) was readily located on a double-pass grating spectrometer which was dried to eliminate water vapor absorption (Figure 1). However, it is rather weak and narrow, and this together with its proximity to a strong water vapor line may explain why it has not been observed previously.

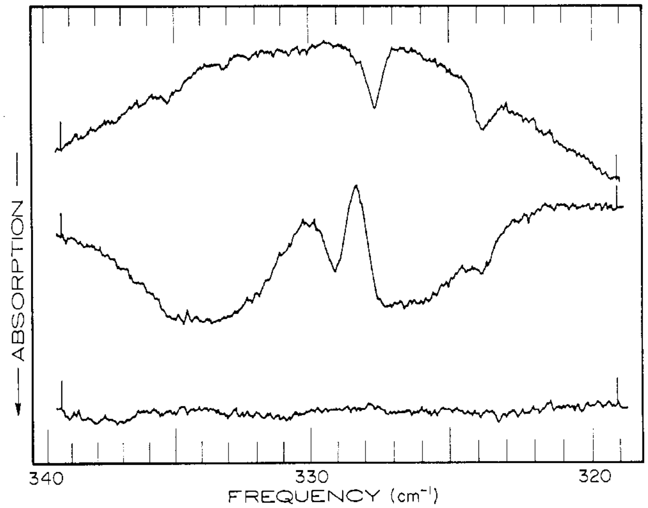

Figure 1.– Contour of ν_4 at 329 cm^{-1}: middle trace, OsO_4 at approximately equilibrium pressure at 25° in a 1-m absorption cell; upper and lower traces, background and zero, respectively. A Perkin-Elmer Model 112G spectrophotometer was used. The two sharp peaks in the background trace are due to water vapor.

(3) Vapor-phase values for the remaining fundamentals are 970 cm^{-1} (ν_1, A_1) and 960.5 cm^{-1} (ν_3, F_2), in substantial agreement with most previous work.[2,4–7] The weak unexplained band at 912 cm^{-1} in the vapor, reported by Hawkins and Sabol[4] but by no subsequent investigators, is real and corresponds to a very weak polarized band in the Raman spectrum. It is presumably the Os–^{18}O stretching vibration (A_1) of the molecule $Os^{18}O^{16}O_3$.

There remains a problem in determining the Coriolis coefficients, and hence the force constants, from the observed band contours. The R and P branch maxima of ν_4 are at 334.0 and 326.3 cm^{-1}, and this 7.7-cm^{-1} spacing yields $\zeta_4 = 0.64$ for $B = 0.1349$ cm^{-1}.[8] The observed ζ sum thus lies in the range 0.7–0.8, compared with a theoretical value of $^1/_2$. Levin and Abramowitz[2] avoid this difficulty by assigning ν_4 a P–R spacing of 12.5 cm^{-1}, but it is obvious from their own published spectrum that the band is not this wide, regardless of how the "missing" Q branch is interpreted. In fact, the discrepancy between the observed and theoretical Coriolis sums lies well outside the experimental error involved in determining the individual coefficients from the band contours. I have no explanation other than the contour of ν_4 is strongly perturbed by the nearby band ν_2, with which it can be in Coriolis interaction. Mills[9,10] has recently emphasized the importance to symmetric-top band contours of such "second-order" Coriolis interactions between nearly degenerate fundamentals. Presumably the same effect obtains here and may account for both the anomalous ζ value and the weakness of the Q branch. If this explanation is correct, the best force constant solution for the F_2 symmetry block would be obtained from the two frequencies and ζ_3, ignoring ζ_4.

However, here we face another difficulty, which is inherent in determining the Coriolis coefficients from unresolved bands: estimates of the P–R spacings of such bands have an appreciable uncertainty which may render them almost useless for determining off-diagonal force constants. Reported values for the P–R spacing of ν_3 for OsO_4 are a case in point: 19.5 ± 0.4 cm^{-1} at 273°K,[7] 19.4 cm^{-1} at 298°K,[4] 19.0 ± 0.5 cm^{-1} at 298°K (this author's value), and 18.5 ± 0.5 cm^{-1} at 309.5°K.[2] These yield Coriolis constants $\zeta_3 = 0.04$, 0.08, 0.10, and 0.14, respectively, with an uncertainty in each case of about ± 0.02; the corresponding values of F_{34} vary from -0.29 to $+0.04$ mdyne/A. Fortunately in this particular case the diagonal force constants are relatively insensitive to F_{34} and we may state with some confidence that $F_{33} = 7.8 \pm 0.1$ and $F_{44} = 0.43 \pm 0.01$ mdyne/A, neglecting anharmonicity.

The force constants obtained by the alternative method of isotopic substitution might aid in clarifying the force field, and the preparation of $Os^{18}O_4$ is in progress here for this purpose.

LOS ALAMOS SCIENTIFIC LABORATORY
UNIVERSITY OF CALIFORNIA
LOS ALAMOS, NEW MEXICO 87544
ROBIN S. MCDOWELL

RECEIVED MARCH 27, 1967

---

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

(5) A. Langseth and B. Qviller, *Z. Physik. Chem.*, **B27**, 79 (1934).

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

(7) R. E. Dodd, *ibid.*, **55**, 1480 (1959).

(8) H. M. Seip and R. Stølevik, *Acta Chem. Scand.*, **20**, 385 (1966).

(9) I. M. Mills, *Pure Appl. Chem.*, **11**, 325 (1965).

(10) C. DiLauro and I. M. Mills, *J. Mol. Spectry.*, **21**, 386 (1966).