

The spectrum in the C≡N stretching region constitutes a good example of how measurements with polarized light permit the assignment of the various vibrations to the symmetry species to which they belong.

In the free ion the C≡N stretching vibrations divide among the symmetry species as follows: $2A_1 + E + B_1$. From Chart I it can be seen that the vibrations of species A_1 are polarized along the a and b axes, the vibrations of species E are polarized along the three axes, and the vibrations of species B_1 are polarized only along the c axis. The spectrum in Figure 2 indicates that the absorption bands observed at 2175 and 2163 cm^{-1} correspond to vibrations of species A_1 , the band at 2145 cm^{-1} corresponds to the vibration of species E , and the band at 2158 cm^{-1} corresponds to the vibration of species B_1 .

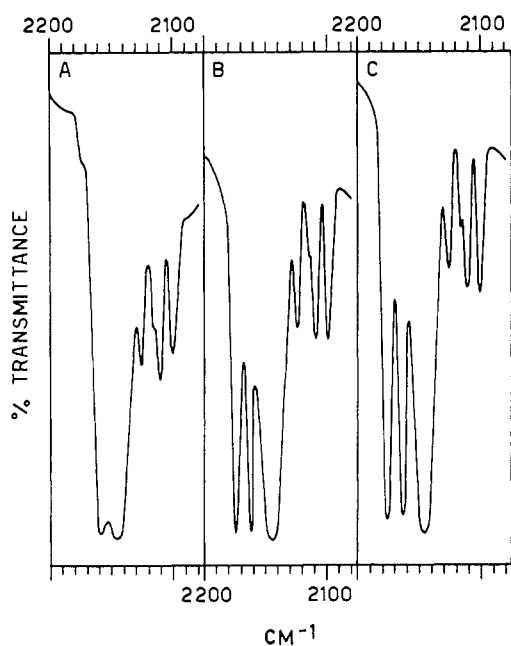


Figure 2.—Infrared spectra in polarized light in the 2200–2100- cm^{-1} region: A, section perpendicular to the a axis, polarization parallel to the c axis; B, section perpendicular to the a axis, polarization parallel to the b axis; C, section perpendicular to the b axis, polarization parallel to the a axis.

The weaker absorption bands observed between 2130 and 2100 cm^{-1} may be attributed to combinations of C≡N fundamentals with lattice vibrations situated at about 45 cm^{-1} or to C≡N stretchings of cyano groups with ^{13}C . The spectrum of $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ in KBr pellets at liquid nitrogen temperature shows a slight increase in intensity and in frequency (about 4 cm^{-1}) both of these bands and of the C≡N fundamentals with respect to the spectrum measured at room temperature. If these bands are combinations of lattice modes with the C≡N fundamentals, they must be difference bands and if so then there are three consequences: (1) sum bands should also be observed; (2) lowering the temperature should reduce the intensity of the difference bands;⁸ (3) since the frequency of lattice vibrations increases markedly by lowering the

(8) The author is indebted to a referee for these two suggestions.

temperature, the frequency of the difference bands should decrease. Since none of these three effects is observed, this explanation seems to be ruled out. Thus it appears reasonable to attribute these bands to C≡N stretchings of cyano groups with ^{13}C .

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

Infrared Detection of Xenon Dichloride

BY LEONARD V. NELSON AND GEORGE C. PIMENTEL

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Thus far, definitive evidence concerning inert gas-halogen compounds has been restricted to fluorides. Rundle and co-workers made encouraging observations that suggested the existence of xenon chlorides.¹ Persistent efforts to exploit this report in the Berkeley laboratories failed to give positive results.² Only very recently has real progress been reported when Meinert³ offered mass spectrometric evidence that he had isolated a compound containing xenon and chlorine, possibly xenon dichloride. Using techniques resembling those of Meinert, we have at last obtained the infrared spectrum of xenon dichloride.

Mixtures of xenon and chlorine ($\text{Xe}/\text{Cl}_2 = 200\text{--}100$) were passed through a microwave discharge (2450 mc, RK 5609, Raytheon Corp.) and then condensed upon a cesium iodide optical window maintained at 20°K. Infrared spectra were then recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer 225 grating infrared spectrophotometer (frequency accuracy, $\pm 0.2 \text{ cm}^{-1}$; spectral slit width, 0.4 cm^{-1}). A broad, structured absorption centered near 313 cm^{-1} was observed which was not observed when chlorine alone passed through the glow discharge. The band was reproduced, however, if xenon was deposited through a separate jet convergent at the cold window with the excited chlorine stream. Figure 1 shows this absorption under optimum resolution.

If the 313- cm^{-1} feature is due to a xenon chloride, then a complex structure can be expected because of the isotopic complexity (xenon has seven isotopes above 1% natural abundance). The hypothesis that the spectrum is due to xenon dichloride can be reasonably tested by attempting to reproduce this spectrum through calculations. Two parameters are needed, a force constant and a characteristic line shape. To fix the force

(1) R. E. Rundle to G. C. Pimentel, private communication, 1963.

(2) See R. D. Spratley, Ph.D. Thesis, University of California, Berkeley, Calif., 1965.

(3) H. Meinert, *Z. Chem.*, **6**, 71 (1966).

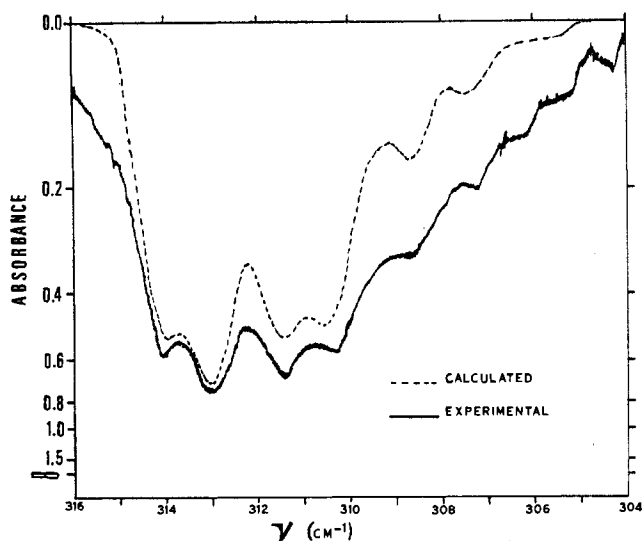


Figure 1.—Infrared spectrum of xenon dichloride.

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 undoubt-

edly absorb below the limit of our spectral range, 200 cm^{-1} . The asymmetric stretching force constant, $k_r - k_{rr}$, is 1.317 mdyne/A , approximately half that of XeF_2 and KrF_2 (respectively, 2.60 and 2.59 mdyne/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
($k_r - k_{rr} = 1.317\text{ mdyne/A}$)

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 Tetroxide¹

Sir:

The recent paper with this title by Levin and Abramowitz² 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) This work was sponsored by the U. S. Atomic Energy Commission.

(1) No trace of the band reported by Levin and Abramowitz² 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} .

(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).