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Vibrational Analysis of SeF_6 and WF_6

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Received July 20, 1966

The gas-phase infrared vibration–rotation spectra of SeF_6 and WF_6 have been measured in the region of their fundamental absorption bands. Coriolis coupling constants, evaluated from the observed contours, are used as constraints for the general force fields for these molecules.

Introduction

Recently, the general force fields of some group VI hexafluorides were determined by supplementing the vibrational secular equation with Coriolis ζ-constant information.[2] Since the separation between P and R branch maxima is a function of the Coriolis constants, these particular vibration–rotation interaction parameters can be reliably determined from vapor-phase infrared band contours.[3-6] In this study, the examination of the vibration–rotation band contours and the determination of intramolecular force fields are extended to SeF_6 and WF_6.

The contours of SeF_6 are of interest since isotopic complications can significantly perturb the band contour of the infrared-active stretching fundamental. The analogous infrared-active stretching mode of WF_6, however, exhibits a well-defined PQR band shape from which a ζ-constant determination can be readily obtained.

The Coriolis data that are calculated for both the selenium and tungsten hexafluorides are combined with the vibrational frequency data to yield a unique potential function for the F_{1u} infrared-active species. Since the two F_{1u} vibrational modes require three symmetry force constants for a complete determination of the potential function, vibrational frequency data alone are inadequate for specifying the normal coordinates.

Experimental Section

SeF_6, synthesized by direct combination of selenium and fluorine in a bomb, contained no infrared-detectable impurities. WF_6 contained SiF_4 as a contaminant. However, the infrared bands of the SiF_4 impurity were in different regions of the spectrum from the WF_6 fundamentals and consequently did not interfere with the band contours of the tungsten species. A Perkin-Elmer Model 521 spectrophotometer, with spectral slit widths of approximately 0.8 cm^{-1}, was used to record the infrared spectra.[7] Conventional 5- and 10-cm demountable metal gas cells were equipped with polyethylene, CsI, and CsBr windows. A low-temperature cell was used to obtain the ν_3 stretching region of SeF_6 at 195°K. The CsI windows were attached to a copper cell through indium wire O rings. The metal cell, surrounded by another evacuated glass cell, was in intimate contact with a solid CO_2 and acetone mixture.

Band Contours

The gas-phase band contour for the ν_4 vibration of SeF_6 exhibits a well-defined PQR structure that is not complicated by the presence of selenium isotopes. The P–R separation for this fundamental is 13.0 ± 0.5 cm^{-1}. However, the ν_3 stretching region, Figure 1a, is complicated by the merging of the P, Q, and R branch absorptions from the naturally abundant selenium isotopes. At 195°K the superposition of the P, Q, and R branches of the individual isotopes is readily observed in the more apparent band structure of the gas, as seen in Figure 1b. A quantitative description of the observed ν_3 region is given below. For the determination of a force field for SeF_6, only ζ_4 was used. A representative trace of the ν_4 vibration appears in Figure 2. The normal PQR structure for the ν_3 vibration of WF_6, Figure 3, yields a P–R branch separation of 12.0 ± 0.5 cm^{-1}.

The traces in Figures 2 and 3 are representative, redrawn scans. The actual separations for the P–R branch maxima, reported in Table I, are averages of numerous expanded infrared scans of necessarily larger scale than those shown in the figures. The P and R branch maxima were determined individually on each of eight to twelve traces for SeF_6 and WF_6, respectively, with the points of maximum intensity of the P and R branches being located visually. The assignment of the P and R branch maxima was repeated independently by a second investigator with reproducible results. Averages of the separations of the maxima for each of the two molecular species indicate that the separation of P and R branch maxima can be determined reliably and within 0.5-cm^{-1} precision. For other molecular systems, as, for example, SF_6, TeF_6, NF_3, PF_3, AsF_3, and BF_3, in which Coriolis ζ constants can be obtained from P–R branch separations for both modes of a degenerate vibrational species, the excellent agreement with the theoretical ζ-sum rules supports confidence in the band contour method of measuring Coriolis constants.[1,4,5]

The P–R frequency separation is related to the Coriolis ζ constant for a degenerate mode of a spherical top molecule by[2]

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

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

[2] S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **44**, 3353 (1966).

[3] (a) W. F. Edgell and R. E. Moynihan, *ibid.*, **27**, 155 (1957); (b) *ibid.*, **45**, 1205 (1966).

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

[5] I. W. Levin and S. Abramowitz, *ibid.*, **44**, 2562 (1966).

[6] S. Abramowitz and I. W. Levin, *J. Mol. Spectry.*, **19**, 461 (1966).

[7] 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.

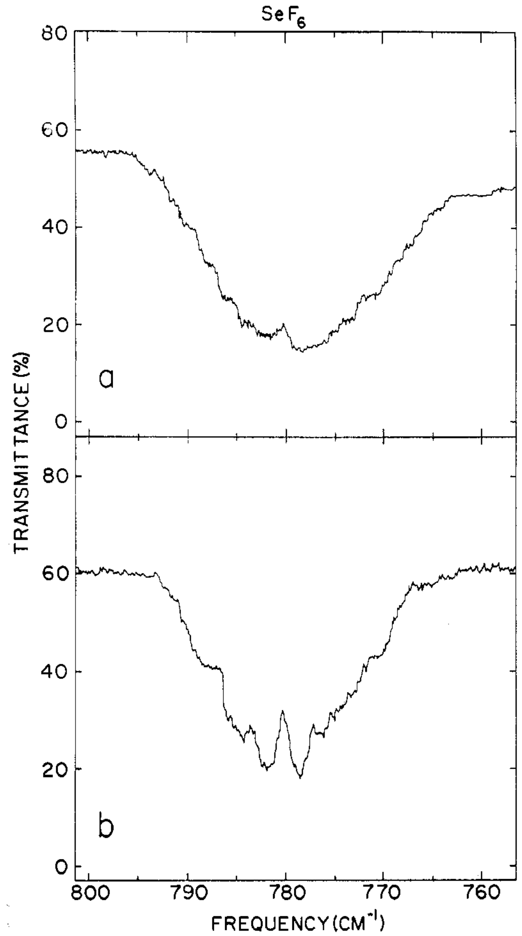

Figure 1.—The vibration–rotation band contour for the ν_3 fundamental of SeF_6: (a) ambient temperature; (b) 195°K.

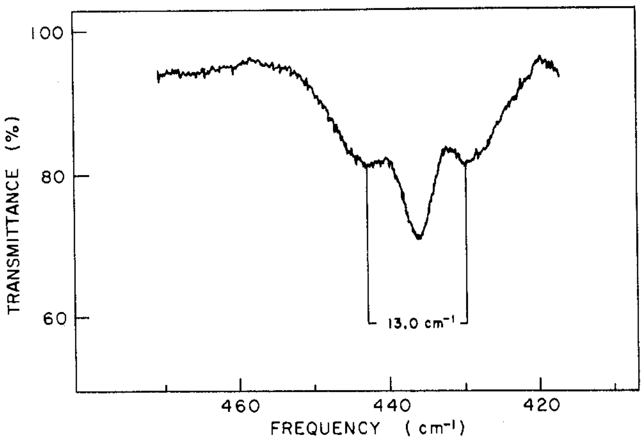

Figure 2.—The vibration–rotation band contour for the ν_4 fundamental of SeF_6.

where $\Delta\nu_{P-R}$ represents the P–R separation in cm^{-1}, B is the rotational constant in cm^{-1}, T is in degrees Kelvin, ζ_i is the Coriolis constant associated with the ith degenerate vibration, and h, k, and c are the fundamental constants. A summary of the observed frequencies, P–R separations, computed Coriolis ζ constants, and bond lengths is given in Table I. The error in the ζ constants for the octahedral fluorides is limited principally by the accuracy with which the P–R branch separations can be measured.[4]

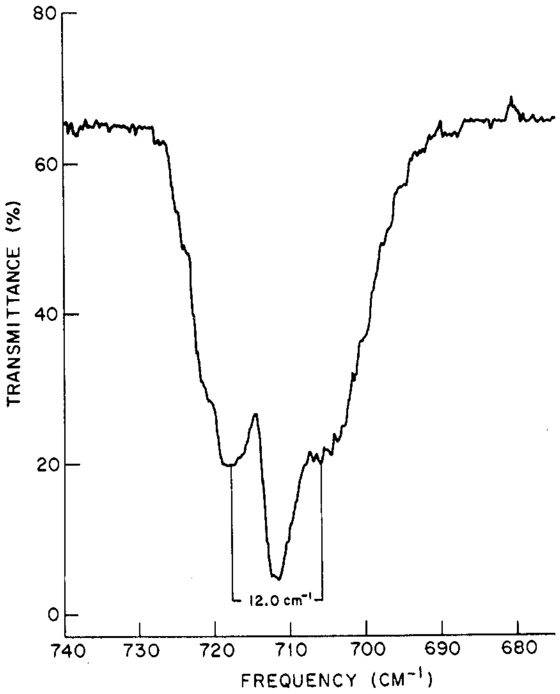

Figure 3.—The vibration–rotation band contour for the ν_3 fundamental of WF_6.

TABLE I

OBSERVED DATA FOR SeF_6 AND WF_6

	Obsd freq, cm^{-1}	$\Delta\nu_{P-R}$, cm^{-1}	ζ_i	Bond length, A
		SeF_6		
ν_3	778.5			1.67[a]
ν_4	436	13.0 ± 0.5	0.21 ± 0.03	
		WF_6		
ν_3	712	12.0 ± 0.5	0.20 ± 0.03	1.826[b]
ν_4	258[c]			

[a] "Tables of Interatomic Distances and Configuration in Molecules and Ions," L. E. Sutton, Ed., The Chemical Society, London, 1958. [b] Footnote *a*, Supplement 1956–1959. [c] Reference 9.

Vibrational Analysis

The ambiguity in the force field calculation for octahedral fluorides occurs in the F_{1u} symmetry species for which the vibrational secular equation was solved to give an exact frequency fit for a wide range of the F_{34} interaction force constants. Since the Coriolis coupling constants are sensitive functions of the force field, a knowledge of the value of ζ_3 or ζ_4 enables a specification of the force constants within rather narrow limits. The ζ-constant dependence to the force field is given by $\zeta = \mathbf{L}^{-1}\mathbf{C}(\mathbf{L}^{-1})'$, where $\mathbf{L}$ represents the transformation from normal coordinates to symmetry coordinates and is given by the eigenvectors of the vibrational secular equation. The $\mathbf{C}$ matrix is a function of the atomic masses and molecular geometry. Plots of the F_{1u} diagonal force constants and Coriolis constants as functions of the interaction force constant for SeF_6 and WF_6 appear in Figures 4 and 5. Thus, these plots represent the numerous possible sets of force constants and ζ values that are consistent with the observed frequency

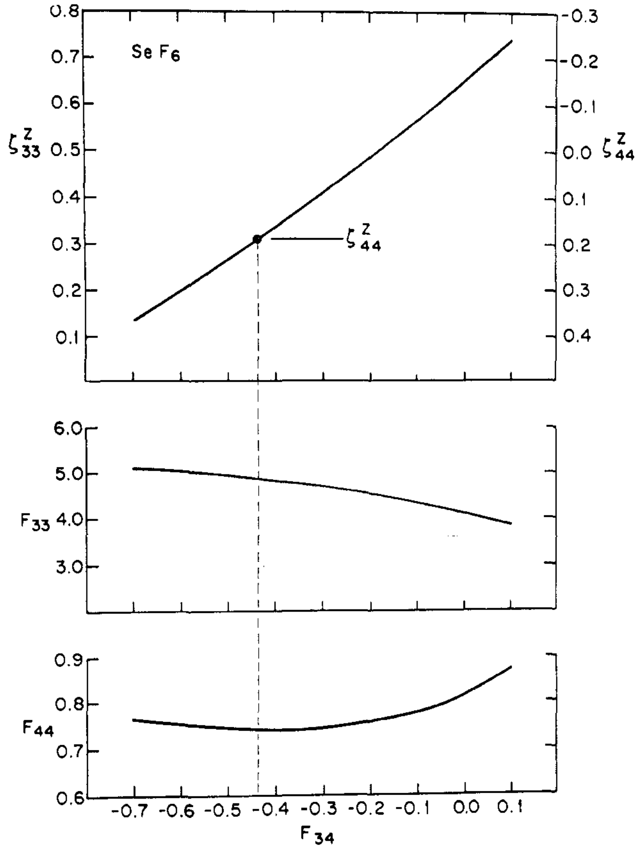

Figure 4.—Plots of F_{33}, F_{44}, ζ^z_{33}, and ζ^z_{44} as functions of F_{34} for the F_{1u} symmetry species of the SeF_6 molecules.

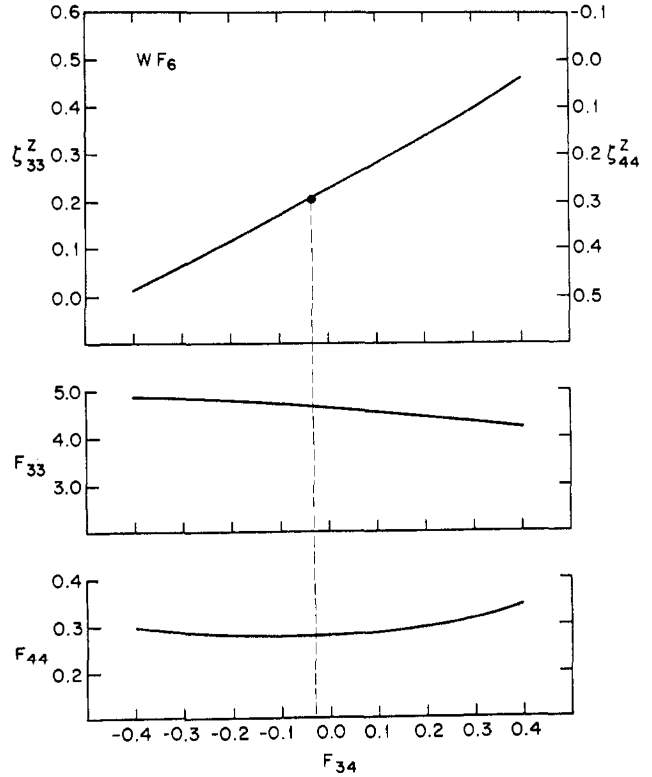

Figure 5.—Plots of F_{33}, F_{44}, ζ^z_{33}, and ζ^z_{44} as functions of F_{34} for the F_{1u} symmetry species of the WF_6 molecules.

data. The details of these calculations are found in ref 2. In Figures 4 and 5 the solid circles represent the experimental Coriolis constants, while the dotted vertical lines designate the preferred F_{1u} species force constants that are determined from the Coriolis data. Table II summarizes the complete force field for the SeF_6 and WF_6 molecules. The force constants for the symmetry species other than F_{1u} were determined by a first-degree equation using the additional data given by Gaunt and Burke, *et al.*[8,9]

The moderate curvatures of the F_{33} and F_{44} curves indicate that frequency data alone can determine reasonable values of the principal force constants. However, we wish to emphasize that F_{34} cannot be determined from only frequency information. This is an important point since normal coordinates, or the vibrational form, are often highly dependent upon the value of interaction force constants. The magnitudes of the F_{33}, F_{44}, and F_{34} force constants for SeF_6 lie between the respective force constants reported for SF_6 and TeF_6.[2] There has not been a complete force field determined for any of the group VIa metal hexafluorides with which one may compare the force constants reported here for WF_6. However, the results of various approximate methods used by other workers to obtain general force fields for the octahedral species have been discussed elsewhere.[2,10–13]

Selenium has six naturally occurring isotopes in abundances varying from 0.96 to 49.96%. The vibrational frequencies of these different molecular species may be expected to differ slightly for these modes in which the central atom vibrates. The spectrum of ν_3 of SeF_6 that is recorded at room temperature, shown in Figure 1a, is, as expected, not resolved into distinct P, Q, and R branches. However, at 195°K the unresolved vibration–rotation band contours for each isotopic species are contracted, according to eq 1; and in Figure 1b, one can see individual Q branches for the different isotopic molecules. Using the derived force field for the F_{1u} species of SeF_6, the resulting vibrational differences for the various isotopes are presented in Table III together with the experimental differences. The ^{80}Se isotope, the most abundant species, occurs at 778.5 cm^{-1}. The good agreement between the calculated and observed vibrational differences for the ν_3 vibration of SeF_6 is gratifying since many of the P, Q, and R branches of the various species are overlapped. For the ν_4 vibration of SeF_6, 74% of the intensity falls within 1.5 cm^{-1}; consequently, one observed a slightly broadened Q branch with typical unresolved P and R branches. A more accurate measurement of the isotopic splittings for these fundamentals might be determined by isolating SeF_6 in an inert matrix at low temperatures, as was done for ν_3 of BCl_3.[14]

One of the more important uses of general force fields is as a basis for evaluating other simplified model force

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(8) J. Gaunt, *Trans. Faraday Soc.*, **49**, 1122 (1953).

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(10) H. H. Claassen, *ibid.*, **30**, 968 (1959).

(11) M. Kimura and K. Kimura, *J. Mol. Spectry.*, **11**, 368 (1963).

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(14) J. J. Comeford, S. Abramowitz, and I. W. Levin, *J. Chem. Phys.*, **43**, 4536 (1965).

TABLE II

FORCE CONSTANTS OF SeF_6 AND WF_6 (MDYNES/A)

		SeF_6		WF_6	
Species	Force constant	General force field	Urey–Bradley force field[a]	General force field	Urey–Bradley force field[a]
A_{1g}	$F_{11} = f_r + 4f_{rr} + f_{rr}'$	5.64	5.64	6.62	6.59
E_g	$F_{22} = f_r - 2f_{rr} + f_{rr}'$	4.90	4.91	5.02	5.04
F_{1u}	$F_{33} = f_r - f_{rr}'$	4.88 ± 0.10	4.41	4.68 ± 0.08	4.90
	$F_{34} = -2(f_{r\alpha} - f_{r\alpha}'')$	−0.44 ± 0.03	−0.20	−0.03 ± 0.04	−0.42
	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha}'' - f_\alpha'''$	0.64 ± 0.01	0.63	0.28 ± 0.01	0.28
F_{2g}	$F_{55} = f_\alpha + f_{\alpha\alpha}''' - 2f_{\alpha\alpha}'$	0.46	0.49	0.29	0.28
F_{2u}	$F_{66} = f_\alpha - 2f_{\alpha\alpha} + 2f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$	0.38	0.35	0.26	0.28

[a] Data from J. Haraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20,** 819 (1964).

TABLE III

ISOTOPIC SPLITTINGS OF THE FUNDAMENTALS OF SeF_6

		ν_3		
Species	Abundance, %	Calcd shift, cm^{-1}	Obsd shift, cm^{-1}	ν_4 calcd shift, cm^{-1}
$^{82}SeF_6$	8.84	−3.0	−2.5	−1.4
$^{80}SeF_6$	49.96	0	0	0
$^{78}SeF_6$	23.61	3.2	3.5	1.5
$^{77}SeF_6$	7.50	4.8	6.0	2.3
$^{76}SeF_6$	9.12	6.5		3.1
$^{74}SeF_6$	0.96	10.0	...	4.6

fields. A comparison is given in Table II between the general force fields which were determined in this work and the modified Urey–Bradley force fields for SeF_6 and WF_6 which were determined by Hiraishi, *et al.*,[15] and more recently by Thakur and Rai.[16] This modified force field, which adds angle and bond interaction constants to the simple Urey–Bradley field, yields reasonable values for the principal force constants for the molecules studied but differs significantly in the interaction force constants F_{34}. Since the Coriolis ζ constants are quite sensitive to values of F_{34}, the modified Urey–Bradley force field is inconsistent with these coupling parameters.

The trends in the F_{1u} force constants for SF_6, SeF_6, and TeF_6 are the same as for the degenerate species of the group IV tetrafluorides and group V trifluorides. The interaction force constant for all three groups has a large negative value which decreases as the mass of the central or unique atom increases. Since WF_6 is the only group VIa hexafluoride for which an unambiguous value of the interaction force constant has been determined, it would be premature to discuss its possible physical significance.

Acknowledgments.—We wish to express our appreciation to Dr. P. A. G. O'Hare, of the Argonne National Laboratory, who kindly synthesized an extremely pure sample of SeF_6 for this study. S. A. wishes to acknowledge the support of the Air Force Office of Scientific Research, U. S. Department of Defense.

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[15] J. Haraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20,** 819 (1964).

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Reactivity of Transition Metal Fluorides. IV. Oxidation–Reduction Reactions of Vanadium Pentafluoride

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Received October 11, 1966

Earlier studies on the comparative reactivities of vanadium, niobium, and tantalum pentafluorides indicated that vanadium pentafluoride was a powerful oxidant. This has been supported by more detailed investigation. Many of the reactions of the pentafluoride with lower fluorides are more complicated than those of corresponding higher fluorides of transition elements, and there is evidence that in these reactions complex formation leads to the production of a fluorovanadium(IV) cation.

Introduction

In the third paper in this series[1] a brief account was given of the reactivity of vanadium pentafluoride. It was shown to be a powerful fluorinating and oxidizing agent. Also, the marked reactivity of vanadium pentafluoride was found to be consistent with its physical properties and its position in the periodic table. Vanadium pentafluoride was found to undergo a number of oxidation–reduction reactions with suitable reagents.

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[1] J. H. Canterford and T. A. O'Donnell, *Inorg. Chem.*, **5,** 1442 (1966).