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Citation: The Journal of Chemical Physics **42**, 1229 (1965); doi: 10.1063/1.1696102 View online: http://dx.doi.org/10.1063/1.1696102 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/42/4?ver=pdfcov Published by the AIP Publishing

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approximated by

quantities:

$$D_{n} = d[S, M, M_{n}, \phi(m)]$$

$$\times d[S, M_{n}, M_{n'}, -\phi'(m)]d[S, M_{n'}, M_{n''}, \Theta]$$

$$\times d[S, M_{n''}, M_{n'''}, \phi'(m-1)]$$

$$\times d[S, M_{n'''}, M', -\phi(m-1)], \quad (AII.19)$$

$$\delta_{n} = \omega_{I} + B(m)M - B(m-1)M'$$

 $+\omega_m(2M_n-2M_n'''+M_n''-M_n').$ (AII.20)

In this more complete expression B(m) and $\phi(m)$ are defined by Eqs. (AII.15) and (AII.13), respectively, while Θ is defined by Eq. (2.43). The expressions for D_k and δ_k are found by replacing the subscript n of these equations with the subscript k.

Since additional variables are needed to express δ_k additional resonance lines are predicted for this more general case. Many of these additional resonance lines are weak and not easily detected. Some would also be predicted by considering higher-order FM sideband components.

Line 7 of Fig. 3 is readily obtained from this more

general case. It is convenient to consider this line using the approximations made in Case II of Sec. 3.4 and stated by Eq. (3.4). It happens that B(m) and $\phi(m)$ given by Eq. (AII.15) and (AII.13) reduce to the

1229

$$\phi'(m) = \frac{1}{2}\beta\gamma_{S}H_{2}/[\omega_{m} + A(m)]. \quad (AII.21)$$

In place of Eq. (3.8), δ_k is approximated by

$$\delta_{k} = \omega_{I} - A(m)M + A(m-1)M' + \omega_{m}[M - M' + 2M_{k} - 2M_{k}''' + M_{k}'' - M_{k}']. \quad (AII.22)$$

values given by Eqs. (3.5) and (3.6), and $\phi'(m)$ is

Line 7 is obtained with $M = -\frac{1}{2}$, $M' = \frac{1}{2}$, and the other variables must be chosen so that the coefficient of ω_m in Eq. (AII.22) is unity. This can be obtained only if

$$M_k = \frac{1}{2}, M_k' = M_k'' = \pm \frac{1}{2}$$
 and $M_k''' = -\frac{1}{2}$.

Substituting these coefficients in Eq. (AII.9) yields

Φ

 $D_n = \cos\left[\frac{1}{2}\Theta\right] \sin\left[\frac{1}{2}\phi(\frac{1}{2})\right] \sin\left[-\frac{1}{2}\phi(-\frac{1}{2})\right] \sin\left[-\frac{1}{2}\Phi'\right],$

where

$$'\equiv\phi'(-\frac{1}{2})-\phi'(-\frac{1}{2}).$$

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 42, NUMBER 4

15 FEBRUARY 1965

Infrared and Raman Spectra of Krypton Difluoride*

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(Received 22 September 1964)

The infrared and Raman spectra of KrF2 vapor have been obtained. They clearly indicate a linear and symmetric molecule with the symmetric stretching frequency at 449 cm⁻¹, the asymmetric stretching frequency at 588 cm⁻¹, and the bending frequency at 232.6 cm⁻¹. The force constants are $f_r = 2.46$, $f_{rr} = -0.20$, and $f_{\alpha} = 0.21$ mdyn/Å. The negative bond-bond interaction constant can be explained neither by valence bond models nor by a simple molecular orbital model.

INTRODUCTION

RYPTON difluoride was first prepared by Turner **K** and Pimentel¹ at low temperature by ultraviolet irradiation of a solid mixture of the elements. The compound was identified and its structure suggested as being linear and symmetric by its two infrared absorption bands at 236 and 580 cm⁻¹. These frequencies are near those of the infrared-active fundamentals of xenon difluoride,² which has been shown to have symmetry $D_{\infty h}$. MacKenzie, who prepared larger quantities of krypton difluoride by electron beam irradiation,³ was able to observe the higher frequency for the vapor as a doublet band with no Q branch and with absorption maxima at 582 and 597 cm^{-1,4} We have now obtained rather complete vibrational spectra for this molecule, including observation of all three fundamentals for the vapor and of one infrared-active binary combination.

EXPERIMENTAL PROCEDURE

The krypton difluoride was prepared as described by Schreiner, Malm, and Hindman.⁵ Samples were sublimed into infrared or Raman cells and then repurified by pumping to a good vacuum while keeping part of

^{*} Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[†] Permanent address: Wheaton College, Wheaton, Illinois.
[†] J. J. Turner and G. C. Pimentel, Science 140, 975 (1963).
² P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, and D. F. Smith, Science 139, 24 (1962).

⁸ D. R. MacKenzie, Science 141, 1171 (1963). ⁴ D. R. MacKenzie (private communication). ⁵ F. Schreiner, J. G. Malm, and J. C. Hindman, J. Am. Chem. Soc. (to be published).





the cell at -78° C. The absorption cell was made of nickel. Polyethylene or AgCl windows were used. Krypton difluoride obviously reacted slowly with the material of the cell. Probably some spontaneous decomposition occurred too. In one experiment with AgCl windows the sample was left in the spectrophotometer at room temperature for 4 h. During this time the absorbance at the peak of the most intense band decreased by 47%. This, of course, was slow enough not to interfere seriously with the measurements. Infrared spectra were obtained with a Beckman IR-7 spectrophotometer using NaCl or CsI prisms. Absorption below 250 cm⁻¹ was measured with a Perkin-Elmer 301 spectrophotometer.

The Raman spectra were observed with a Cary-81 spectrophotometer, using mercury excitation at 4358 Å. The crystalline krypton difluoride was contained in a 7-mm-o.d. Pyrex tube with a rounded end. For the gaseous sample a 22-mm-o.d. Pyrex tube with a plane window was used in connection with the optical system designed for 19-mm tubes. A sufficient quantity of the difluoride was placed in the cell to obtain the saturation vapor pressure at 30°C and still have solid left in a sidearm.

RESULTS

Figure 1 shows a tracing of the infrared spectrum of krypton difluoride covering the region from 200 to 1100 cm⁻¹. The most intense absorption bands are centered at 232.6 and 588 cm⁻¹, the former exhibiting PQR structure while the latter displays only the P and R branches. A third but weaker band is located at 1032 cm⁻¹.

In addition to the absorption bands already named there are four lines in the region between 200 and 400 cm⁻¹, marked with X's, a very weak absorption band at 703 cm⁻¹, and a band at 733 cm⁻¹ which is also marked with an X. The four lines are part of the rotational spectrum of hydrogen fluoride originating from a reaction of the sample with the polyethylene windows of the cell, as is evident from the fact that they grew in intensity during successive scans of this region. The frequency and shape of the very weak absorption band at 703 cm⁻¹ coincide with the strongest absorption band of chlorine trifluoride,⁶ and it is reasonable to assume that this compound is formed within the infrared cell by a reaction of the krypton difluoride with the silver chloride windows. The absorption band at 733 cm⁻¹ appears only faintly in the tracing of the first scan (upper curve) but shows up more prominently in the tracing of a later scan of this part of the spectrum (lower curve). Its frequency corresponds to the strongest absorption band of chlorine pentafluoride reported by Smith,⁷ and its appearance here is evidence for the strong fluorinating power of krypton difluoride.

Figure 2 is a tracing of the Raman spectrum of the solid krypton difluoride. The very intense and unusually narrow appearance of a band at 462.3 cm^{-1} together with the relatively high vapor pressure of the



FIG. 2. Raman spectrum of Solid KrF₂. Slitwidth: A, 8 cm⁻¹; B, 4 cm⁻¹; C, 2 cm⁻¹.

⁶ H. H. Claassen, B. Weinstock, and J. G. Malm, J. Chem. Phys. 28, 285 (1958). ⁷ D. F. Smith, Science 141, 1039 (1963).

Infrared spectrum		Raman spectrum	Interpretation	Description		
2	32.6 s		<i>v</i> ₂	Degenerate bending mode		
		449 (vapor) 462.3 (solid)	ν_1	Symmetric stretching mode		
5 5	$\begin{pmatrix} 80\\96 \end{pmatrix}$ 588 vs		ν_3	Asymmetric stretching mode		
1	032 m		$\nu_1 + \nu_3 = 1037$			

TABLE I. Vibrational frequencies of KrF_2 and their interpretation. (All frequencies given in cm⁻¹.)

compound (it is estimated to be well above 100 mm Hg at room temperature) encouraged us to attempt the measurement of the symmetric stretching frequency for the vapor. This Raman experiment was successful and resulted in the trace shown in Fig. 3. The measured frequency of 449 cm⁻¹ for the molecule in the gas phase is probably accurate to within 1 or 2 cm⁻¹.

INTERPRETATION

The observed vibrational frequencies for KrF_2 are listed in Table I. This table also contains our assignments of these frequencies for the vapor in terms of the usual notations for a symmetric, linear, triatomic molecule, YZ₂. The activities of both fundamental and combination bands in the infrared and Raman spectra, as well as the shape of all the infrared absorption bands are in complete accordance with this model. This constitutes overwhelming evidence that the molecules of krypton difluoride in the vapor phase are linear and symmetric. This result was, of course, to be expected on the basis of the similar results obtained for xenon difluoride.²

Only one binary combination band is observed in the infrared spectrum, viz., $\nu_1 + \nu_3$. Another combina-



FIG. 3. Raman spectrum of KrF₂ vapor. Slitwidth: 10 cm⁻¹.

tion band is to be expected at $682 \text{ cm}^{-1} (=\nu_1+\nu_2)$. Observation in this region of the spectrum is difficult because of overlapping with the 703 cm⁻¹ ClF₃ band; window material other than AgCl should be used in an attempt to observe the frequency of this combination band.

The spectroscopic data presented in this paper do not permit a precise calculation of the bond length r_0 in krypton difluoride. An estimate can be given, however, along the following lines. For xenon difluoride the Xe-F bond length has been estimated by Smith⁸ from the separation of the P and R branches in the infrared absorption band of ν_3 . He found a $\Delta \nu$ of 16 cm⁻¹ for the pure compound, and a $\Delta \nu$ of 14.2 \pm 0.2 cm⁻¹ for a mixture of XeF_2 with fluorine, the rotational lines being pressure-broadened in the latter case. The smaller $\Delta \nu$ corresponds to a Xe–F bond length of 1.9 Å. In the case of the krypton diffuoride we find a $\Delta \nu$ of 15.5 ± 0.5 cm⁻¹ for the pure compound. We conclude, therefore, that within the experimental uncertainty of 0.1 A XeF_2 and KrF_2 have equal distances between the central and the fluorine atoms. Xenon difluoride has a bond length of 2.00 Å in the solid state⁹ and 1.9 Å in the vapor phase as noted above. Consequently, the figure $r_0 = 1.9 \pm 0.1$ Å may be given as an estimated value for the Kr-F distance in gaseous krypton difluoride.

The force constants for krypton difluoride, calculated with the assumption that the band origins coincide with the observed band centers are: $f_r=2.46$, $f_{rr}=$ -0.20, and $f_{\alpha}=0.21$, all in millidynes per angstrom unit. These constants are defined by the following equation for twice the potential energy:

$$2V = f_r(\Delta r_1^2 + \Delta r_2^2) + 2f_{rr}\Delta r_1\Delta r_2 + r_0^2 f_\alpha \Delta \alpha^2,$$

where Δr_1 and Δr_2 are changes in the bond distances and $\Delta \alpha$ is the change in bond angle. The values are listed in Table II along with those of XeF₂, BrF₃, and ClF₃. The last two are **T**-shaped plane molecules in which two of the fluorine atoms are nearly opposite each other. Bonding in the noble gas fluorides has been compared to that in these interhalogen compounds¹⁰

1231

⁸ D. F. Smith, in *Noble-Gas Compounds*, edited by H. H. Hyman (University of Chicago Press, Chicago, Illinois, 1963), p. 297. ⁹ H. A. Levy and P. A. Agron, J. Am. Chem. Soc. **85**, 241

^{(1963).} ¹⁰ K. S. Pitzer, Science **139**, 414 (1963).

	Frequencies (cm ⁻¹)			Force constants (mdyn/Å)		
Molecule	ν ₁	V2	ν3	fr	frr	f_{α}
 KrF2	449	232.6	588	2.46	-0.20	0.21
${ m XeF_2}$	515	213.2	558	2.84	0.13	0.20
ClF3ª	529	345ь	703	2.90	0.23	0.32
BrF₃ª	531		613	3.00	0.15	

TABLE II. Comparison of frequencies and force constants.

^a Frequencies taken from Ref. 6.

^b The mean between the in-plane and out-of-plane bending frequencies.

by considering the central Cl-F and Br-F groups to be comparable to noble gas atoms. The force constants for the two halogen fluorides are approximate ones since they were calculated by looking only at the nearly linear part of the molecule. The frequencies for these motions are only approximately known⁶ because in the larger molecules they mix to some extent with other modes.

A striking feature of the force constants for krypton difluoride is the negative value of its bond-bond interaction constant, f_{rr} . This negative value indicates that in krypton difluoride it is easier to lengthen or to shorten both bonds simultaneously than it is to lengthen one bond and to shorten the other. This feature of the molecule sets it apart from xenon difluoride and from other linear symmetric triatomic molecules in general. Valence bond descriptions of molecules of this type seem to yield positive values for the interaction constant f_{rr} . We have therefore investigated a particularly simple molecular orbital description of the type used by Lohr and Lipscomb¹¹ and based on Mulliken's magic formula, in the hope that this approach would be sufficiently simple to be understood but sufficiently discriminating to explain the change in the sign of f_{rr} . The calculated interaction constants were uniformly positive and about an order of magnitude larger than those observed for these molecules. This failure of our simple molecular orbital calculation probably arises from one or more of the following three crudities of the method employed:

(1) Interaction energies between orbitals were approximated as the sum of orbital energies times the overlap of these orbitals.

(2) Only four molecular orbitals, two of symmetry σ_{g}^{+} and two of symmetry σ_{u}^{+} , were considered. These orbitals are occupied by six electrons in the ground state of xenon difluoride or of krypton difluoride.

(3) No account was taken of any correlation between the motions of electrons occupying the same molecular orbital.

The interpretation of the negative bond-bond interaction constant of krypton difluoride remains an inter-

esting problem, and it seems unlikely that it will be solved by an intuitive or easily understood calculation.

Another unusual feature in the vibrational spectra of krypton difluoride that deserves some comment is the blue shift in its Raman-active frequency that takes place when the vapor is condensed to a pure, solid phase at room temperature. In the vapor this frequency is 449 cm⁻¹, but in the solid it is 462.3 cm⁻¹. A red shift on condensation is much more usual for a primarily stretching vibrational frequency of a molecular crystal. For example, in the case of xenon difluoride the Raman-active frequency changes from 515 cm⁻¹ in the vapor to 497 cm⁻¹ in the solid.⁸ Moreover, the Raman scattering usually observed from solid samples of molecular crystals is much broader than that observed here for krypton difluoride.

These surprising features in the Raman spectrum of pure, solid krypton difluoride are made more understandable by the fact that the x-ray powder patterns obtained at room temperature with krypton difluoride¹² show that it is not isostructural with xenon difluoride.⁹ A complete analysis of the crystal structure for krypton difluoride has, however, not yet been worked out. On the basis of the unusual behavior of the Raman-active frequency for this compound, it seems that our conclusions about the molecular structure of krypton difluoride in the vapor phase will not be directly applicable to the solid phase at room temperature.

There is one final question on which we want to comment. This question was raised by Lord.13 The question is, Why doesn't one see a Fermi-resonance interaction between the frequencies ν_1 and $2\nu_2$, both of which come in the neighborhood of 460 cm⁻¹? The answer to this question seems to be that the frequency difference here, $2\nu_2 - \nu_1$, some 16.2 cm⁻¹ for gaseous krypton difluoride, is large enough to overwhelm the influence of those anharmonic terms in the molecular potential function that tend to produce an interaction between these two otherwise normal modes. The comparable frequency differences in two classic cases of Fermi resonance,14 carbon dioxide and carbon tetrachloride, are 2 and 4 cm⁻¹, respectively.

¹¹L. L. Lohr and W. N. Lipscomb, in Ref. 8, p. 347.

¹² S. Siegel and E. Gebert, J. Am. Chem. Soc. 86, 3896 (1964).

 ¹³ R. C. Lord (private conversation with H. H. Classen).
 ¹⁴ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), pp. 274, 311.