

THE MICROWAVE SPECTRUM AND STRUCTURE OF KRYPTON–PHOSPHORUS TRIFLUORIDE*

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ABSTRACT

The rotational spectrum of the weak complex between krypton and phosphorus trifluoride has been observed using a Fourier transform microwave spectrometer with a pulsed supersonic nozzle molecular beam source. The complex is an asymmetric top. The distance r_{cm} between the krypton atom and the center of mass of the PF_3 molecule is 4.0722 Å and the angle between the r_{cm} vector and the C_3 axis of the PF_3 is 68.25°. Based on the centrifugal distortion constant D_J and a pseudodiatomic model, the binding energy of the complex is estimated to be 218 cm^{-1} .

INTRODUCTION

The weak complex between argon and PF_3 was recently reported to be an asymmetric top [1]. The distance between the centers of mass of Ar and PF_3 was $r_{\text{cm}} = 3.9533$ Å; the angle between r_{cm} and the PF_3 symmetry axis was 70.30°.

The present study was undertaken to determine if the greater size and polarizability of krypton would lead to any significant structural changes in its complex with PF_3 and to compare the strength of the interaction with PF_3 as the rare gas atom is varied.

EXPERIMENTAL

The rotational spectrum was observed with a Fourier transform cavity microwave spectrometer with both Newport BV-100 and Bosch fuel injector pulsed nozzle gas sources. The spectrometer details are reported elsewhere [1,2]. The preexpansion gas was composed of about 50–90% neon or argon, 8–49% krypton and 1–2% PF_3 at pressures from 0.5 to 2 atm. Samples containing the larger ratios of Kr gave better signals. With carefully selected timing the Doppler

*Dedicated to Prof. D.S. Millen on the occasion of his retirement.

splitting of the transitions was usually not resolved. Typical linewidths (FWHM) were 8–12 kHz and line centers were reproducible to 1 kHz. Several of the very low- J transitions were somewhat broader, probably due to unresolved spin hyperfine structure from the phosphorus and fluorine nuclei. No effects from internal rotation of the PF_3 were seen. The strongest transitions of $^{84}\text{Kr}\cdot\text{PF}_3$ could be observed with a S/N of about 2/1 with a single gas pulse. Mixing experiments clearly showed that Kr and PF_3 were necessary to observe the spectrum. Mass spectral analysis of the PF_3 sample (PCR Inc.) indicated that impurities were below 0.1%.

SPECTRA AND ANALYSIS

The spectrum consisted of strong c -dipole and weaker a -dipole transitions. The assigned transitions of the ^{84}Kr (56.9% natural abundance) and ^{86}Kr (17.4%) isotopes are given in Table 1. The forty transitions for the more abundant isotope could be fit with a standard deviation of 2 kHz using a Watson S -reduction (I') hamiltonian with seven distortion constants. Only the five P^4 distortion constants were well determined for the less abundant isotope and the standard deviation of the fit was 2.6 kHz. The spectral parameters are given in Table 2.

The value of $P_{bb} = \sum m_i b_i^2$ is also given in Table 2. The nearly identical values for the two isotopic species and their similarity to the value in free PF_3 (52.6513 amu \AA^2) indicate that the Kr lies in a plane of symmetry (C_s point group). The differences between the PF_3 value and those of the complex presumably arise from vibrational effects although small changes in the PF_3 geometry cannot be ruled out. If these small differences are ignored, the distance between Kr and the center of mass of the PF_3 moiety (r_{cm}) as well as the angle between r_{cm} and the symmetry axis of the PF_3 can then be determined by least-squares fitting of the 6 moments of inertia and 3 principal axes conditions while constraining the structure of the PF_3 to its reported value [3]. This gives $r_{\text{cm}} = 4.0722 \text{ \AA}$ and $\theta = 68.25^\circ$ with an r.m.s. deviation in the fitted moments of 0.091 amu \AA^2 . These parameters correspond to the so-called r_o structure [3]. This structure gives Kr coordinates of $a_o = 2.0838 \text{ \AA}$ and $c_o = 0.0394 \text{ \AA}$ which compare well with the substitution values determined from Kraitchman's equations [4], $a_s = 2.0765 \text{ \AA}$ and $c_s = 0.0332 \text{ \AA}$.

While the differences are small between the r_o and r_s coordinates and between P_{bb} for the complex and free PF_3 , vibrational effects are probably significant and will affect the conversion of r_{cm} and θ into equilibrium values. A rough estimate using a pseudodiatomic model (see below) indicates that the equilibrium value of r_{cm} will be about 0.03 \AA shorter. The equilibrium value of θ may also be affected by a few degrees. A more complete analysis of the centrifugal distortion constants may be able to provide additional insight on this question.

A comparison with Ar- PF_3 is given in Table 3. The increase in r_{cm} upon

TABLE 1

Observed and calculated rotational transitions for Kr·PF₃ (MHz)

$J' (K'_p, K'_o)$	$J (K_p, K_o)$	ν^a		$\Delta\nu^b$	
		$^{84}\text{Kr}\cdot\text{PF}_3$	$^{86}\text{Kr}\cdot\text{PF}_3$	$^{84}\text{Kr}\cdot\text{PF}_3$	$^{86}\text{Kr}\cdot\text{PF}_3$
1(1,0)	0(0,0)	7866.058	0.004	7858.692	0.005
2(1,1)	1(0,1)	9167.133	0.003	9145.646	0.003
3(1,2)	2(0,2)	10482.334	0.000	10446.425	-0.002
4(1,3)	3(0,3)	11811.741	-0.001	11761.109	-0.001
5(1,4)	4(0,4)	13155.498	-0.003	13089.831	-0.001
6(1,5)	5(0,5)	14513.816	-0.003	14432.792	-0.001
7(1,6)	6(0,6)			15790.254	-0.003
7(0,7)	6(0,6)	8902.512	0.000	8808.122	-0.001
7(1,7)	6(1,6)	8806.698	0.002	8714.248	0.001
7(1,6)	6(1,5)	9005.500	0.001	8908.844	0.000
7(2,6)	6(2,5)	8905.525	0.000	8810.971	0.001
7(2,5)	6(2,4)	8910.660	0.002	8815.887	0.003
7(3,5)	6(3,4)	8905.190	0.002	8810.612	0.002
7(3,4)	6(3,3)	8905.207	-0.004	8810.627	-0.005
7(4,4)	6(4,3)	8902.359	0.000		
8(0,8)	7(0,7)	10171.812	0.000	10064.027	-0.002
8(1,8)	7(1,7)	10063.723	0.001	9958.097	0.002
8(1,7)	7(1,6)	10290.847	0.001	10180.419	0.004
8(2,7)	7(2,6)	10176.784	0.001	10068.747	0.000
8(2,6)	7(2,5)	10184.478	0.000	10076.112	-0.001
8(3,6)	7(3,5)	10176.919	0.000		
8(3,5)	7(3,4)	10176.966	0.001		
9(0,9)	8(0,8)	11440.123	0.001	11318.981	0.001
9(1,9)	8(1,8)	11320.321	0.000	11201.530	0.000
9(1,8)	8(1,7)	11575.727	-0.001	11451.535	-0.001
9(2,8)	8(2,7)	11447.658	-0.001	11326.151	-0.001
9(2,7)	8(2,6)	11458.642	0.001	11336.666	0.001
9(3,7)	8(3,6)	11448.471	0.000		
9(3,6)	8(3,5)	11448.555	-0.001		
4(1,3)	3(2,1)	14502.434	-0.002		
4(1,4)	3(2,2)	14786.202	-0.001		
5(1,4)	4(2,2)	13159.632	0.001	13251.022	-0.005
5(1,5)	4(2,3)	13584.554	0.000		
6(1,5)	5(2,3)	11803.767	-0.001	11910.388	0.001
6(1,6)	5(2,4)	12397.307	0.001	12491.434	-0.001
7(1,6)	6(2,4)	10435.408	-0.002	10557.484	0.001
7(1,7)	6(2,5)	11224.539	-0.001	11330.058	0.004
8(1,7)	7(2,5)	9055.223	0.000		
8(1,8)	7(2,6)	10066.347	0.004		
9(1,9)	8(2,7)	8922.803	-0.002		

^aObserved frequency.^bObserved - calculated frequency.

TABLE 2

Spectroscopic constants for Kr·PF₃

	⁸⁴ Kr	⁸⁶ Kr
<i>A</i>	7215.6640(13)MHz	7215.3575(18)MHz
<i>B</i>	650.6089(2)	643.5480(2)
<i>C</i>	622.1812(2)	615.7218(2)
<i>D_J</i>	1.361(1)kHz	1.338(1)kHz
<i>D_{JK}</i>	25.37(3)	25.12(2)
<i>D_K</i>	162.3(4)	162.3(5)
<i>d₁</i>	-61.3(4)Hz	-60.0(7)Hz
<i>d₂</i>	-6.4(3)	-6.0(5)
<i>H_{JK}</i>	-1.2(6)	
<i>H_{KJ}</i>	-14.5(9)	
<i>P_{bb}</i>	52.76523 Amu Å ²	52.76605 Amu Å ²

TABLE 3

Derived parameters for rare-gas-PF₃ complexes

	Kr·PF ₃	Ar·PF ₃
<i>r_{cm}</i>	4.0722 Å	3.9533 Å
<i>θ</i>	68.25°	70.30°
<i>k_s</i>	0.0191 mdyn Å ⁻¹	0.0165 mdyn Å ⁻¹
<i>ω_s</i>	27.5 cm ⁻¹	32.0 cm ⁻¹
<i>ε</i>	218 cm ⁻¹	176 cm ⁻¹

replacing Ar with Kr is about 0.12 Å which is similar to the increase of 0.10–0.11 Å for the hydrogen halide [5,6] and OCS [7,8] rare gas complexes while in contrast to the values of 0.06 Å and 0.18 Å for the ClF [9] and HCN [10] complexes, respectively. The decrease in *θ* of about 2.2° in the Kr complex is interesting; however it is not large enough, given the uncertainty in vibrational averaging effects, to signify clearly that the equilibrium value of *θ* is different between the Kr and Ar complexes. The values of the force constants and vibrational frequencies for the weak stretching mode between the rare-gas atom and PF₃ were estimated from the centrifugal distortion constant *D_J* using the pseudodiatomic model with the relationship:

$$k_s = 8 \pi^4 (\mu r_{cm})^2 (B+C)^4 / h D_J$$

By assuming a Lennard–Jones 6/12 potential to describe the angle averaged radial interaction, the well depth *ε* was also estimated [6]. The values of *ε* for the two PF₃ complexes are compared to a number of other rare gas complexes

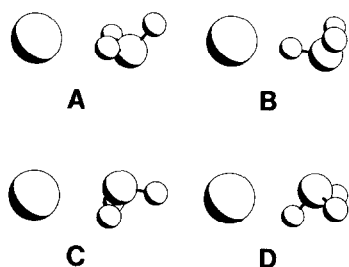
in Table 4. It is apparent that the interaction energy of the PF_3 complexes is approximately in the middle of the range compared to other rare-gas complexes.

Because of the symmetry of the PF_3 , the experimental rotational constants of Kr-PF_3 (and Ar-PF_3) cannot shed light on the internal orientation of the PF_3 moiety. Figure 1 illustrates the four conformations which are consistent with the experimental data. However, structure B is very unlikely since the Kr-F distance is 2.72 Å which is 0.8 Å shorter than the sum of their van der Waals' radii. The Kr-F distance is 3.01 Å in structure D which also appears too short given the small interaction energy. The structures A and C both have plausible Kr-F distances of 3.54 Å and 3.77 Å, as well as Kr-P distances of 4.28 Å and 3.91 Å, respectively. Since neither phosphorus nor fluorine have any other stable isotopes, it is not possible to definitively resolve this ambiguity with additional inertial data. Preliminary ab initio fixed geometry calculations of Ar-PF_3 at the 6-21G level with second-order Møller-Plesset corrections

TABLE 4

Bond lengths and potential well depths for various rare-gas complexes

	R_{CM} (Å)	ϵ (cm^{-1})	Ref.
Ar-SO ₃	3.350	390	11
Ar-Furan	3.54	236	12
Kr-ClF	3.963	289	10
Ar-ClF	3.905	228	10
Kr-PF ₃	4.072	218	
Ar-PF ₃	3.953	176	
Ar-OCS	3.706	176	13
Ar-ClCN	3.649	168	14
Ar-BF ₃	3.325	159	15
Ar-CO ₂	3.433	143	11
Ar-O ₃	3.42	104	16
Kr-HCl	4.111	179	6
Ar-HCl	4.006	128	6
Kr-HBr	4.257	165	6
Ar-HBr	4.146	89	6

Fig. 1. Conformations of $\text{Kr}\cdot\text{PF}_3$ which are consistent with the observed rotational constants.

(MP2) also were not definitive [1]. They placed structure C 100 cm^{-1} above structure A (which was the only bound conformation – total energy $\approx 80\text{ cm}^{-1}$ less than the sum of the Ar and PF_3 energies). However the small energy difference and the nature of the calculation do not warrant a firm conclusion and so the conformational details of rare-gas– PF_3 complexes are considered unresolved at this point.

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