THE MICROWAVE SPECTRUM OF ARGON–PHOSPHORUS TRIFLUORIDE

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The argon–PF_3 complex has been prepared in a supersonic expansion of Ar (98%) and PF_3 (2%). A Fourier-transform microwave spectrometer employing a Fabry–Pérot cavity was used to assign 28 rotational transitions. The rotational constants (MHz) and distortion constants (kHz) were $A=7332.468(10)$, $B=1023.055(2)$, $C=952.564(2)$, $D_J=3.53(1)$, $D_{JK}=60.4(1)$ and $d_1=-0.240(7)$. The argon atom is 3.953 Å (r_{cm}) from the PF_3 center of mass and r_{cm} makes an angle of 70.3° with the C_3 axis of the PF_3.

1. Introduction

Several van der Waals complexes with a high atom percentage of fluorine have been studied by high-resolution techniques. Examples include BF_3–N_2 [1], HCF_3 bonded to an acid or ammonia [2,3], COF_2–Ar [4], ClF–Ar [5], and a number of HF complexes [6]. Most of the systems are linear or symmetric tops. Usually the fluorine atoms are distant from the second species and do not appear to directly interact with it. Ar–COF_2 is an exception; it is an asymmetric top (of necessity) with the Ar located above the CF_2 triangle. We report here the microwave spectrum of the Ar–PF_3 complex which is also an asymmetric top. In this complex, the fluorine is closer than phosphorus to the argon atom.

2. Experimental

The spectrum was observed with a Fourier-transform microwave spectrometer of the Balle–Flygare type [7] with a pulsed nozzle gas source. The spectrometer operated in the region of 8–18 GHz with a HP 8671B synthesizer as the MO. The microwave cavity employed aluminum mirrors with a diameter of 35 cm and radius of curvature of 85 cm separated by ≈60 cm. A semicircular wire loop (≈1 cm diameter) was used as the transmitting and receiving antenna. Heterodyne techniques converted the coherent MW emission to a low-frequency signal which was sampled at 1024 points at 200 or 500 ns intervals by a Datalab DL910 transient recorder (eight-bit resolution). The FID signal was transferred to a PDP-11/23 computer where signal averaging of up to 100000 shots and the Fourier transformation were carried out. A Newport BV-100 pulsed nozzle and driver were used with a pulse repetition rate of about 6 Hz (limited by the data transfer rate to the computer). The nozzle orifices were 0.5 and 1.0 mm and the backing pressure was typically 1–2 atm (≈98% Ar, 2% PF_3). Doppler splitting of the lines [8] was minimized by controlling the pulse timing to examine the leading edge of the gas pulse entering the cavity. Typical linewidths of ≈8 kHz were observed except in some very-low-J transition where hyperfine interactions appeared to complicate and broaden the line shape.

3. Spectra and analysis

The first transitions were observed in a spectral region predicted for a symmetric top Ar–PF_3 complex. Gas mixing and purity tests indicated that both Ar and PF_3 were essential for observation of the spectrum. However, subsequent searches could not identify the additional transitions expected for a

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Table 1
Observed and calculated rotational transitions for Ar–PF_3 (MHz)

$J'(K'_p,K'_0)$	$J(K_p,K_0)$	Freq. (obs.)	Freq. (calc.)	Calc. – obs.
1(1,0)	0(0,0)	8355.380	8355.387	0.007
2(1,1)	1(0,1)	10401.150	10401.150	0.000
3(1,2)	2(0,2)	12482.069	12482.068	−0.001
4(1,3)	3(0,3)	14598.771	14598.768	−0.003
5(1,4)	4(0,4)	16752.300	16752.299	−0.001
8(0,8)	7(1,6)	8364.500	8364.499	−0.001
9(0,9)	8(1,7)	9999.103	9999.103	0.000
10(0,10)	9(1,8)	11578.049	11578.051	0.002
4(0,4)	3(0,3)	7895.704	7895.705	0.001
4(1,3)	3(1,2)	8040.831	8040.828	−0.003
4(2,3)	3(2,2)	7899.198	7899.185	−0.013
4(2,2)	3(2,1)	7905.048	7905.054	0.006
5(0,5)	4(0,4)	9864.608	9864.605	−0.003
5(1,5)	4(1,4)	9697.088	9697.085	−0.003
5(1,4)	4(1,3)	10049.236	10049.236	−0.000
5(2,4)	4(2,3)	9872.633	9872.613	−0.020
5(2,3)	4(2,2)	9884.323	9884.340	0.017
5(3,3)	4(3,2)	9872.875	9872.885	0.010
5(3,2)	4(3,1)	9872.940	9872.949	0.009
6(0,6)	5(0,5)	11830.173	11830.175	0.002
6(1,6)	5(1,5)	11634.069	11634.068	−0.001
6(1,5)	5(1,4)	12056.425	12056.428	0.003
6(2,5)	5(2,4)	11845.155	11845.129	−0.026
6(2,4)	5(2,3)	11865.582	11865.622	0.040
7(0,7)	6(0,6)	13791.773	13791.779	0.006
7(1,7)	6(1,6)	13569.750	13569.752	0.002
7(1,6)	6(1,5)	14062.136	14062.146	0.010
7(2,6)	6(2,5)	13816.587	13816.552	−0.035

symmetric top species. Asymmetric models with the Ar swinging 180° between the two ends of the PF_3 molecule were then examined and led to a successful search for confirmatory transitions. A total of 28 μ_a and μ_c transitions were assigned. They are listed in table 1. The derived rotational constants and centrifugal distortion constants are given in table 2. The D_J and D_{JK} constants are approximately 2–3 times smaller than for the Ar–COF_2 species [4]. No evidence for internal rotation of the PF_3 was observed.

Table 2
Spectroscopic constants for Ar–PF_3 [a]

A = 7332.468(10) MHz	D_J = 3.53(1) kHz
B = 1023.055(2) MHz	D_{JK} = 60.4(1) kHz
C = 952.564(2) MHz	d_1 = −0.240(7) kHz

[a] Distortion constants from van Eijk–Typke–Watson S-reduction [9], representation I^r.

Transition intensities for $J=7$ and $J=8$ levels ($E \approx 2$ cm^{-1}) began to fall off presumably due to the low rotational temperature in the molecular beam. Hyperfine structure was partially resolvable for several low-J transitions ($J \leqslant 2$) due to the presence of phosphorus ($I=1/2$) and two kinds of fluorine atoms ($I=1/2$). The complexity of the coupling precluded an analysis at this stage.

The value of $I_a+I_c-I_b=105.3186$ amu Å^2 is close to the value expected (105.3027 amu Å^2) for two fluorine atoms straddling a plane of symmetry based on the structure of free PF_3 [10]. The discrepancy between the observed and ideal value is smaller than often observed for van der Waals complexes where large-amplitude vibrational motions usually contribute more noticeable vibration–rotation interaction effects. With the assumption of a plane of symmetry and no change in PF_3 structural parameters upon

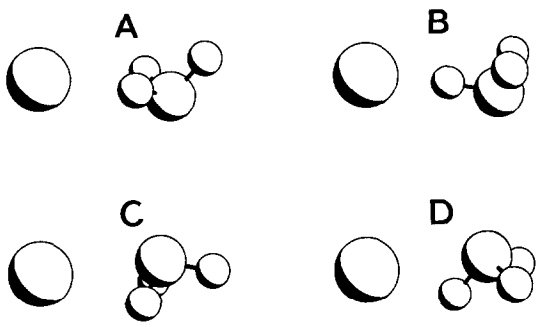

Fig. 1. Conformations of Ar–PF_3 which are compatible with the observed rotational constants.

adduct formation, two additional parameters can be determined, viz. the distance of the argon atom from the center of mass of the PF_3 moiety ($r_{c.m.}$) and the angle (θ) between $r_{c.m}$ and the PF_3 symmetry axis. The program STRFIT originally written by Schwendeman [10] and revised by us was used to analyze the moments of inertia. The resultant fit ($\Delta I_{calc} - \Delta I_{obs} = 0.0709$ amu Å^2) gave $\theta = 70.3°$ and $r_{c\,m} = 3.9533$ Å. Because of the symmetry of PF_3, its orientation relative to the Ar is ambiguous. The four conformations which are consistent with the data are illustrated in fig. 1. Conformation A is transformed into B by a rotation of 180° (or 60°) about the C_3 axis of the PF_3. Conformations C and D result by inverting the PF_3 in A and B through its center of mass.

It is interesting that the four structures each suggest a different interaction. The Ar appears to interact with two fluorines in A, with one fluorine in B, with a PF_2 face in C and roughly with a PF bond in D. Conformation B is considered unlikely since the Ar–F distance is 2.590 Å or about 0.75 Å shorter than the sum of the van der Waals radii. Conformation D also has a somewhat short Ar–F distance (2.856 Å) although this is not so clearly an implausible value. In conformations A and C the Ar–F distance is 3.430 and 3.636 Å, respectively. The Ar–P distance is 4.149 Å in A and B and 3.814 Å in C and D. It is not possible to resolve the structural ambiguity by investigating additional isotopic species. Phosphorus and fluorine have only one stable isotope and ^{36}Ar substitution would not provide any additional structural information even if it could be observed.

Preliminary ab initio fixed geometry calculations [11] at the 6-21G level with second-order Møller–Plesset corrections (MP2) to the correlation energy gave the following relative energy ordering: A = 0 cm^{-1}, C = 109 cm^{-1}, D = 206 cm^{-1}, B = 878 cm^{-1}. Only conformation A was bound (total energy ≈ 80 cm^{-1} less than the sum of the Ar and PF_3 energies). It is difficult to judge the usefulness of this approach apart from another indicator that B is implausible. The calculated energy differences between the other three conformers are not large and small changes in geometries could alter the ordering. More work is planned to explore this question.

This study demonstrates that argon forms a weak complex with PF_3 in which fluorine is closer than phosphorus to the argon. In contrast, Ar binds to the more positive species [12] in the linear Ar–Cl–F complex. One resolution of this paradox arises from application of the proposal that van der Waals molecules mimic the structures of their isoelectronic chemical analogs [5,13]. This would suggest that conformation C with the phosphorus lone pair and two fluorines in pseudoequatorial positions of a trigonal bipyramid is the preferred arrangement. We intend to examine the Ar–PF_2Cl complex as a means to further explore this question.

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