

The microwave spectrum and structure of the neon-phosphorus trifluoride complex

Kurt W. Hillig II, Marabeth S. LaBarge¹, Amine Taleb-Bendiab and Robert L. Kuczkowski

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA

Received 9 April 1990; in final form 22 May 1990

Symmetric top spectra were observed for the ²⁰Ne·PF₃ and ²²Ne·PF₃ van der Waals dimers using a Fourier-transform microwave spectrometer. The center-of-mass distance between Ne and PF₃ is 3.373(3) Å. The experimental data, in conjunction with the van der Waals radii of the atoms and with ab initio calculations, are consistent with the neon atom on the symmetry axis over the F₃ face of the PF₃. Normal mode analysis of the van der Waals vibrations based on the centrifugal distortion constants yields force constants $f_R = 0.00647$ m dyn Å⁻¹ and $f_\theta = 0.00464$ m dyn Å for the ²⁰Ne·PF₃ isotopic species.

The Ar·PF₃ and Kr·PF₃ van der Waals complexes have been thoroughly investigated [1] by Fourier-transform microwave (FTMW) spectroscopy. Both of these complexes have C_s symmetry; dipole moment data and the ⁸³Kr nuclear quadrupole coupling constants show that the rare gas atom lies over a PF₂ face in both species. We have now identified the spectrum of the Ne·PF₃ complex and find it to have C_{3v} symmetry with the neon lying on the threefold axis.

The microwave spectrum of Ne·PF₃ was observed in a FTMW spectrometer [2] while investigating the PF₃·H₂O system with neon as the carrier gas [3]. A number of transitions were found which exhibited first- and second-order Stark effects in the characteristic pattern of a symmetric top. These lines were visible in the absence of H₂O but disappeared when argon was substituted for neon; no additional unassigned lines requiring both Ne and PF₃ were observed. Optimum conditions for visibility were 0.1%–0.5% PF₃ in neon at a total pressure of 3.5–4 atm. The transitions were assigned to the ²⁰Ne·PF₃ and ²²Ne·PF₃ species and are listed in table 1. Both quartic and sextic centrifugal distortion terms were needed to fit the spectrum to experimental accuracy;

the derived rotational and centrifugal distortion constants are given in table 2.

As Ne·PF₃ is a symmetric top, the neon atom must lie along the symmetry axis of the PF₃. Assuming that the PF₃ structure [4] is unchanged upon complexation, the distance of the neon atom from the PF₃ center-of-mass ($R_{c.m.}$) is 3.3746 Å in ²⁰Ne·PF₃ and 3.3704 Å in ²²Ne·PF₃. The difference presumably arises from small changes in vibrational amplitudes upon isotopic substitution. There are two choices for the neon position – over the phosphorus atom or over the F₃ face. The van der Waals radii of Ne, F, and P are about 1.54, 1.47, and 1.80 Å, respectively [5]. For the neon over the phosphorus atom, the P–Ne distance would be 2.875 Å, nearly 0.5 Å too short for a van der Waals interaction. With the neon over the F₃ face, the F–Ne distances are 3.385 Å and the P–Ne distance is 3.873 Å, all 0.4–0.5 Å longer than the sum of the van der Waals radii but reasonable for a very weakly interacting system.

Millen's improved pseudodiatom model for the van der Waals stretching motion [6] in a C_{3v} dimer gives a force constant of $f_s = 16 \pi^2 \mu B_0^3 (1 - B_0/B_m) / D_J$ ^{#1}, where μ is the reduced mass and B_m is the B -

¹ Current address: Dow Chemical Co., Midland, MI 48667, USA.

^{#1} The symbols "k" and "f" are both used by various authors to indicate a harmonic force constant. Where refs. [1,7] use f_{qq} , we use f_s here as in ref. [6]. Similarly, both "ν" and "ω" have been used for frequencies.

Table 1

Assigned transitions of $^{20}\text{Ne}\cdot\text{PF}_3$ and $^{22}\text{Ne}\cdot\text{PF}_3$

J'	K'	J''	K''	$^{20}\text{Ne}\cdot\text{PF}_3$		$^{22}\text{Ne}\cdot\text{PF}_3$	
				ν_{obs} (MHz) ^{a)}	$\nu_{\text{obs}} - \nu_{\text{calc}}$	ν_{obs} (MHz) ^{a)}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
2	0	1	0	8081.284	-0.0004	7643.0665	0.0004
2	1	1	1	8079.353	0.0004	7641.3235	-0.0004
3	0	2	0	12119.494	0.0016	11462.364	0.0011
3	1	2	1	12116.579	-0.0020	11459.735	-0.0016
3	2	2	2	12107.923	0.0004	11451.925	0.0005
4	0	3	0	16154.769	-0.0001	15278.967	0.0003
4	1	3	1	16150.861	0.0001	15275.440	-0.0006
4	2	3	2	16139.239	0.0003	15264.952	0.0004
4	3	3	3	16120.206	-0.0001	15247.768	-0.0001

^{a)} Experimental uncertainty is ± 0.001 – 0.002 MHz.

Table 2

Rotational and distortion constants of $^{20}\text{Ne}\cdot\text{PF}_3$ and $^{22}\text{Ne}\cdot\text{PF}_3$

	$^{20}\text{Ne}\cdot\text{PF}_3$	$^{22}\text{Ne}\cdot\text{PF}_3$
B_0 (MHz)	2020.64507(70) ^{a)}	1911.06418(58)
D_J (kHz)	40.464(75)	37.176(62)
D_{JK} (kHz)	482.13(19)	434.76(16)
H_J (Hz)	-5.2(23)	-4.7(19)
H_{JK} (Hz)	-231.9(74)	-216.9(61)
H_{KJ} (Hz)	1056.3(115)	931.7(95)

^{a)} Uncertainties are 1σ in the last digit.

rotational constant of free PF_3 (7819.99 MHz [8]). Assuming a Lennard-Jones 6–12 potential, the binding energy $\epsilon = (f_s r_e^2 / 72) \approx (f_s R_{c.m.}^2 / 72)$. The derived structural and vibrational parameters are listed in table 3 along with corresponding values for $\text{Ar}\cdot\text{PF}_3$ and $\text{Kr}\cdot\text{PF}_3$ for comparison. Since the zero-point energy $\frac{1}{2}\omega_s$ is nearly 15% of the Lennard-Jones binding energy, it is likely that anharmonic effects will be significant, explaining the difference in force constants between the ^{20}Ne and ^{22}Ne isotopic species.

A more complete description of the van der Waals vibrations may be obtained from a normal mode analysis, including the vibrational motion and force constants of the PF_3 , as described recently for $\text{Ar}\cdot\text{PF}_3$ and $\text{Kr}\cdot\text{PF}_3$ [1]. This uses both $D_J (= -\frac{1}{4}\hbar^4 \tau_{xxxx})$ and $D_{JK} (= -2D_J - \frac{1}{2}\hbar^4 [\tau_{xxzz} + 2\tau_{zzxx}])$ and includes both the stretching and the doubly degenerate van der Waals bending modes; the off-diagonal force constants between these are zero by symmetry. The symmetry coordinate for the stretch is taken as

$\Delta S_1 = \Delta R_{\text{Ne-P}}$ while for the bending these are defined as $\Delta S_2 = (2\theta_1 - \theta_2 - \theta_3) / \sqrt{6}$ and $\Delta S_3 = (\theta_2 - \theta_3) / \sqrt{2}$, where θ_1 is the Ne–P–F₁ angle, etc. The results of this analysis are also listed in table 3. The stretching force constant and frequency are nearly identical to their pseudodiatomic values, verifying the separability of the van der Waals modes from the higher frequency PF_3 motions. Notable is the very small bending force constant and low bending frequency. The differences between the isotopic species again arise from the assumptions of a harmonic potential and small vibrational amplitudes; the rms stretching amplitude $\Delta R_{\text{rms}} = \langle \Delta R^2 \rangle^{1/2}$ is 0.20 Å, while the bending amplitude is 8°. The difference between the effective ($R_{c.m.}$) and average ($R_{c.m.}^*$) Ne– PF_3 distances is 0.01 Å, somewhat larger than the 0.005–0.006 Å seen in the argon and krypton complexes.

The dipole moment was determined by measuring the second-order Stark effects of the $2_0 \leftarrow 1_0$, $M_J = 0$ and 1, and the $2_1 \leftarrow 1_1$, $M_J = 0$ lines of $^{20}\text{Ne}\cdot\text{PF}_3$ at electric field values between 0 and 600 V cm⁻¹. The $2_{0,2} \leftarrow 1_{1,1}$ line (12256.5835 MHz) of a trace of added SO_2 was used as a field calibration standard ($\mu(\text{SO}_2) = 1.63305$ D [10]). The Stark shifts of the SO_2 and dimer lines were measured sequentially at each field value. Fitting the three M_J components independently gave essentially identical values for the dipole moment; averaging the three gives $\mu(\text{Ne}\cdot\text{PF}_3) = 1.0125(10)$ D. This is some 0.016 D smaller than in free PF_3 [1]. This small decrease may arise from an induced dipole moment in the neon atom of 0.016 D antiparallel to the PF_3 dipole mo-

Table 3
Structural and vibrational parameters of $^{20}\text{Ne}\cdot\text{PF}_3$ and $^{22}\text{Ne}\cdot\text{PF}_3$

	$^{20}\text{Ne}\cdot\text{PF}_3$	$^{22}\text{Ne}\cdot\text{PF}_3$	Ar·PF ₃ ^{a)}	Kr·PF ₃ ^{a)}
$R_{\text{c.m.}}$ (Å)	3.3746	3.3704	3.9533	4.0722
θ_0 ^{b)} (deg)	180.0	180.0	70.30	68.25
f_s ^{c)} (mdyn Å ⁻¹)	0.00646	0.00654	0.01647	0.01913
ω_s ^{c)} (cm ⁻¹)	25.9	25.1	31.9	27.5
ϵ (cm ⁻¹)	102.2	103.3	186.6	225.9
f_R ^{d)} (mdyn Å ⁻¹)	0.00647	0.00655	0.01649	0.01933
f_θ ^{d)} (mdyn Å)	0.00464	0.00477	0.01090	0.01537
f_ϕ ^{d)} (mdyn Å)	–	–	0.01615	0.01797
ω_R ^{d)} (cm ⁻¹)	26.0	25.1	31.8	27.6
ω_θ ^{d)} (cm ⁻¹)	13.7	13.7	18.1	20.9
ω_ϕ ^{d)} (cm ⁻¹)	–	–	19.6	20.3
ΔR_{rms} ^{d)} (Å)	0.200	0.197	0.153	0.136
$\Delta\theta_{\text{rms}}$ ^{d)} (deg)	8.0	7.9	10.2	9.7
$\Delta\phi_{\text{rms}}$ ^{d)} (deg)	–	–	7.1	6.8
$R_{\text{c.m.}}^*$ ^{d)} (Å)	3.3847	3.3801	3.9595	4.0774

^{a)} Ref. [1].

^{b)} θ_0 is the P–X–RG angle, where X is the center of mass of the PF₃ and RG is the rare-gas atom.

^{c)} Calculated using the pseudodiatomic model of ref. [6].

^{d)} Calculated from a normal mode analysis (see text). R refers to the stretching coordinate, analogous to f_s ; θ refers to the symmetric (in-plane) bend and ϕ to the asymmetric bend (PF₃ torsion) for Ar·PF₃ and Kr·PF₃. $R_{\text{c.m.}}^*$ is the average center of mass distance [9].

ment. Alternatively, it can be explained by a vibrational averaging of the projection of $\mu(\text{PF}_3)$ onto the C₃ axis of the complex. Estimating the average bending angle as $\cos^{-1}[\mu(\text{PF}_3\cdot\text{Ne})/\mu(\text{PF}_3)]$ gives $\langle\Delta\theta\rangle = 10.3^\circ$; the good agreement with the vibrational analysis above suggests that the induced dipole moment in the neon is somewhat less than 0.016 D.

To further explore the change in the dipole moment, an ab initio calculation on free PF₃, using the GAUSSIAN 86 package with a 6-31G* basis set [11], was used to determine the electric field at the neon site. The use of ab initio calculations on the free polar species has been successful at modeling both electric fields (i.e. dipole moments) and field gradients (via ⁸³Kr nuclear quadrupole coupling) in a number of polar–nonpolar van der Waals complexes [1,7,12]. A map of the calculated field around PF₃ is shown in fig. 1. It is interesting to note that the Ar and Kr sites both exhibit a large positive electrostatic potential while the Ne site has a negative potential. The calculated field at the neon site combined with the polarizability of neon (0.364 Å³ [13]) predicts an induced dipole moment of only 0.0003 D, suggesting

that vibrational averaging rather than polarization accounts for most of the decrease in the dipole moment of the complex.

The small induced moment and negative site polarity both suggest that electrostatic interactions contribute little to the binding in Ne·PF₃. An upper limit to the polarization contribution to the binding energy can be set by assuming that all of the change in the dipole moment arises from polarization of the rare-gas atom, and that higher-order induced moment terms are small compared to the induced dipole contribution. The interaction energy is then $\Delta E = -\mu_{\text{ind}}^2/2\alpha$ [14], where μ_{ind} is the induced dipole moment and α is the polarizability in the rare-gas atom. For the neon, argon and krypton complexes this gives stabilization energies of –1.6, –16.6 and –17.7 cm⁻¹, respectively, confirming the small electrostatic interaction in Ne·PF₃.

To further explore the interactions in this system, a series of HF/SCF ab initio calculations was made on the Ne·PF₃ supermolecule using the 6-31+G* basis set (the diffuse exponent for Ne was set to 0.125), with some smaller basis sets also used. Due

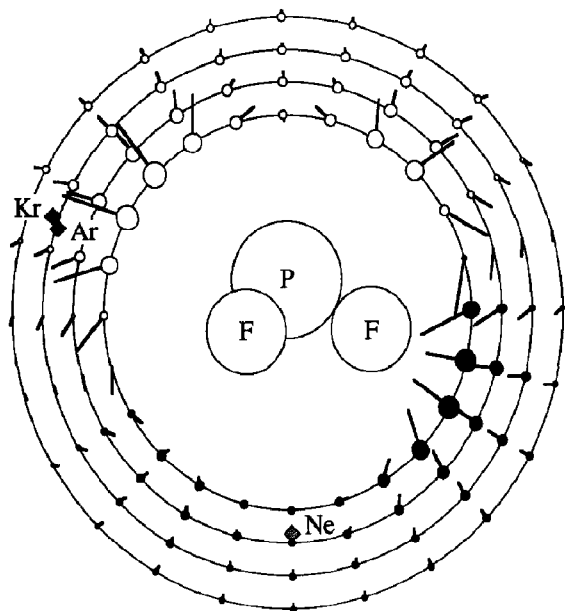


Fig. 1. A map of the electric field around PF_3 . Open circles indicate a positive electrostatic potential and filled circles a negative potential; the magnitude is indicated by their size. The lines indicate the direction and magnitude of the field. Values are calculated at $R_{\text{c.m.}} = 3.0, 3.5, 4.0$ and 4.5 \AA with 15° increments in θ . The locations of Ne, Ar and Kr in their respective complexes are indicated.

to CPU time constraints, MP and CI calculations were not feasible. The potential energy curve calculated for a C_{3v} geometry with the neon over the F_3 face is shown in fig. 2. The minimum energy structure ($\Delta E \approx -20 \text{ cm}^{-1}$) was at $R_{\text{c.m.}} = 3.5\text{--}3.6 \text{ \AA}$; no minimum was found for neon over the P atom. Given the level of the calculations (SCF with diffuse orbitals) it seems reasonable to believe that the electrostatic interactions in the complex will be fairly well modeled but the dispersion interactions will not; the very small binding energy found is consistent with this interpretation. It is interesting in this context that we find a second minimum of nearly equal energy for a structure with the neon over the PF_2 face, roughly at the site predicted by analogy to $\text{Ar}\cdot\text{PF}_3$ and $\text{Kr}\cdot\text{PF}_3$.

There has been some debate in the literature over the utility of the counterpoise correction to eliminate basis set superposition error (BSSE) [15]; the large polarization + diffuse orbital basis set was used in the hope of minimizing BSSE without the computa-

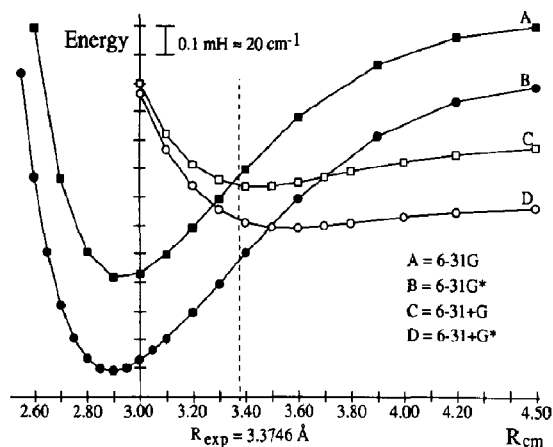


Fig. 2. The ab initio energy versus $R_{\text{c.m.}}$ for $\text{Ne}\cdot\text{PF}_3$ in a C_{3v} geometry, calculated with the 6-31+ G^* basis set. The total dimer energy at $R_{\text{c.m.}} = 4.50 \text{ \AA}$ is -767.62911152 hartree.

tional burden of counterpoise calculations. Trial counterpoise calculations were done for the C_{3v} geometries of $\text{PF}_3\cdot\text{Ne}$; somewhat surprisingly, no minimum in the potential energy could be found.

As the electrostatic contribution to the binding energy in $\text{Ne}\cdot\text{PF}_3$ is small it is clear that the dispersion interactions dominate here, necessitating a more extensive theoretical treatment including electron correlation for an accurate description. Nevertheless it is attractive to rationalize the structures of the rare-gas PF_3 complexes as a balance of polarization and dispersion interactions. In the argon and krypton complexes the larger size and higher polarizabilities force the atom into a site of large field, positive potential, and contact with three of the partner's atoms. For $\text{Ne}\cdot\text{PF}_3$ the neon atom nestles into the open face of the PF_3 pyramid allowing a dispersion interaction with all four partner atoms.

This work has been supported by grants from the National Science Foundation, Washington DC. We appreciate several helpful comments made by the referee.

References

- [1] A. Taleb-Bendiab, M.S. LaBarge, L.L. Lohr, R.C. Taylor, K.W. Hillig II, R.L. Kuczkowski and R.K. Bohn, *J. Chem. Phys.* 90 (1989) 6949.

- [2] K.W. Hillig II, J. Matos, A. Scioly and R.L. Kuczkowski, *Chem. Phys. Letters* 133 (1987) 359.
- [3] K.W. Hillig II, M.S. LaBarge, R.K. Bohn and R.L. Kuczkowski, unpublished work.
- [4] M.D. Harmony, V.W. Laurie, R.L. Kuczkowski, R.H. Schwendeman, D.A. Ramsey, F.J. Lovas, W.J. Lafferty and A.G. Maki, *J. Phys. Chem. Ref. Data* 8 (1979) 619.
- [5] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [6] D.J. Millen, *Can. J. Chem.* 63 (1985) 1477.
- [7] J.J. Oh, K.W. Hillig II, R.L. Kuczkowski and R.K. Bohn, *J. Phys. Chem.*, in press.
- [8] A.M. Mirri, F. Scappini and F.G. Favero, *Spectrochim. Acta* 21 (1965) 965.
- [9] D.R. Herschbach and V.W. Laurie, *J. Chem. Phys.* 37 (1962) 1668.
- [10] D. Patel, D. Margolese and T.R. Dyke, *J. Chem. Phys.* 70 (1979) 2740.
- [11] M.J. Frisch, J.S. Binkley, H.B. Schlegel, K. Raghavachari, C.F. Melius, R.L. Martin, J.J.P. Stewart, F.W. Bobrowicz, C.M. Rohlfing, L.R. Kahn, D.J. DeFrees, R. Seeger, R.A. Whiteside, D.J. Fox, E.M. Fluder and J.A. Pople, *GAUSSIAN 86*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA (1986).
- [12] A.M. Andrews, A. Taleb-Bendiab, M.S. LaBarge, K.W. Hillig II and R.L. Kuczkowski, *J. Chem. Phys.*, submitted for publication; unpublished results.
- [13] R.H. Orcutt and R.H. Cole, *J. Chem. Phys.* 46 (1967) 697.
- [14] E.A. Moelwyn-Hughes, *Physical chemistry*, 2nd Ed. (Pergamon Press, New York, 1961) p. 310.
- [15] S.F. Boys and F. Bernardi, *Mol. Phys.* 19 (1970) 553; D.W. Schwenke and D.G. Truhlar, *J. Chem. Phys.* 82 (1985) 2418; S.K. Loushin, S.-Y. Liu and C.D. Dykstra, *J. Chem. Phys.* 82 (1985) 2720; M.M. Szczyński and S. Scheiner, *J. Chem. Phys.* 84 (1986) 6328.