

## MOLECULAR STRUCTURE OF $\text{Pt}(\text{PF}_3)_4$ BY GAS-PHASE ELECTRON DIFFRACTION

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### ABSTRACT

The structure of  $\text{Pt}(\text{PF}_3)_4$  was reinvestigated making use of a new theory of intramolecular dynamic scattering. Derived molecular parameters were insensitive to the dynamic corrections. Refinements for this tetrahedral molecule yielded  $r_g(\text{Pt}-\text{P}) = 2.229(5)$  Å,  $r_g(\text{P}-\text{F}) = 1.550(4)$  Å, and  $\angle \text{PtPF} = 118.9^\circ(0.4)$ , with the indicated uncertainties representing  $2.5\sigma$ . Amplitudes of vibration were also determined. Diffraction patterns were consistent with freely rotating  $\text{PF}_3$  groups.

### INTRODUCTION

For over a decade it has been observed that systematic discrepancies between experimental and calculated intensities arise in electron-diffraction studies of molecules with heavy atoms even when partial wave scattering factors are used [1]. Recently a theory of intramolecular multiple scattering has been proposed [2–5] which accounts at least in part for the discrepancy found for octahedral molecules. It seemed worth-while to examine the tetrahedral molecule  $\text{Pt}(\text{PF}_3)_4$  from the standpoint of dynamic corrections as well as for the structural information itself. Partial results of a previous, conventional electron diffraction analysis of this molecule have already been reported by Marriott et al. [6].

### PROCEDURE

A sample of  $\text{Pt}(\text{PF}_3)_4$  was used as obtained from Pressure Chemical Company. Its purity was claimed to be at least 98%, the remaining component being arsenic dissolved in the liquid  $\text{Pt}(\text{PF}_3)_4$ . Diffraction patterns were taken of the vapor issuing from a 0.27 mm diameter nozzle at a vapor pressure of about 4 torr corresponding to the liquid at  $-30^\circ\text{C}$ . Exposure times for the 21-cm and 11-cm camera lengths were 16 s and 60 s respectively, with a beam current of  $0.56 \mu\text{A}$ . Patterns were recorded on 4 in  $\times$  5 in Kodak Electron Image plates through a 4.8 cm  $r^3$  sector. Exposures  $E$  were calculated from absorbances  $A$  assuming that  $2\alpha A = [1 - \exp(-2\alpha E)]$  with  $\alpha = 0.1$ .

## ANALYSIS OF DATA

Three 21-cm and four 11-cm patterns were selected for analyses. Indices of resolution for the two data ranges were found to be 0.91 and 0.87, respectively, before the data were blended for final refinements. Levelled experimental intensities  $I_0(s)$  and the background function  $I_B(s)$  for the two camera geometries are available from ASIS\*.

Two independent refinements were carried out, one by conventional procedures [7] and one with inclusion of dynamic scattering corrections as described elsewhere [2, 8]. Elastic and inelastic scattering factors and phase shifts calculated by Schäfer et al. [9] were used throughout the analysis. The determination of the bond lengths and mean-square amplitudes of vibration for  $\text{Pt}(\text{PF}_3)_4$  was done by least squares analysis of the experimental intensities.

No attempt was made to determine the barrier of rotation for the tetrahedrally oriented  $\text{PF}_3$  groups with respect to each other. The  $\text{PtP}_4$  skeleton was assumed to have  $T_d$  symmetry. A series of rotational isomers was constructed which yielded a spectrum of long  $\text{F} \cdots \text{F}$  and  $\text{P} \cdots \text{F}$  distances corresponding to free rotation. Because of the diffuseness of the radial distribution curve in the vicinity of these distances, the refinement was insensitive to the amplitudes assigned to the long  $\text{F} \cdots \text{F}$  distances in the individual isomers in the structure model. Assigning values from 0.2 Å to 0.5 Å for the skeletal root-mean-square amplitude of vibration had no noticeable effect on the agreement between theory and experiment. A value of 0.2 Å was adopted in both structure refinements.

## RESULTS

The final values of the bond lengths and mean-square amplitudes of vibration derived from both analyses are listed in Table 1. Correlation coefficients from the error matrix are given in Table 2. Experimental and theoretical reduced molecular intensity functions  $sM(s)$  are plotted in Fig. 1. It is evident in the residuals for the two separate runs that the dynamic scattering corrections for  $\text{Pt}(\text{PF}_3)_4$  are of minor consequence for this particular molecule, even though rather marked effects had been observed in comparable or even lighter molecules such as  $\text{ReF}_6$  [1-4, 8] and  $\text{XeOF}_4$  [8, 9]. Inclusion of the dynamic corrections decreased the residuals marginally. Derived bond lengths were insensitive to the corrections but some amplitudes of vibration increased slightly. The results of the study do not differ significantly from those determined by Marriott et al., who also

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TABLE 1

Molecular Parameters for Pt(PF<sub>3</sub>)<sub>4</sub>

|                                     | I <sup>a</sup>        | II <sup>b</sup> | III <sup>c</sup> |
|-------------------------------------|-----------------------|-----------------|------------------|
| $r_g(\text{Pt}-\text{P})$           | 2.229(5) <sup>d</sup> | 2.229(6)        | 2.230            |
| $r_g(\text{P}-\text{F})$            | 1.550(4)              | 1.551(4)        | 1.546            |
| $\angle \text{F}-\text{P}-\text{F}$ | 98.6(0.5)             | 98.6(0.5)       | 98.9             |
| $l_g(\text{Pt}-\text{P})$           | 0.050(3)              | 0.050(3)        | —                |
| $l_g(\text{P}-\text{F})$            | 0.042(3)              | 0.042(3)        | —                |
| $l_g(\text{F} \cdots \text{F})$     | 0.070(8)              | 0.065(8)        | —                |
| $l_g(\text{Pt} \cdots \text{F})$    | 0.089(8)              | 0.089(8)        | —                |
| $l_g(\text{P} \cdots \text{P})$     | 0.123(17)             | 0.105(20)       | —                |
| $l_g(\text{P} \cdots \text{F})$     | 0.186(50)             | 0.163(45)       | —                |
| $\sigma(I_o)/\bar{I}_o^e$           | 0.0019                | 0.0012          | —                |

<sup>a</sup>Dynamic corrections applied.<sup>b</sup>Dynamic corrections not applied.<sup>c</sup>Ref. 6.<sup>d</sup>All estimated uncertainties include random and the following systematic errors and correspond to 2.5 $\sigma$ . Errors for wavelength, camera distance measurement, and radial measurement in microphotomentering are estimated to be 3, 3 and 2 parts per ten thousand respectively.<sup>e</sup>Sigma based on uniform weighting of  $sM(s)$ .

TABLE 2

Correlation coefficients for Pt(PF<sub>3</sub>)<sub>4</sub><sup>a</sup>

|                                      | $r_g(\text{P}-\text{F})$ | $\angle \text{Pt}-\text{P}-\text{F}$ | $l_g(\text{Pt}-\text{P})$ | $l_g(\text{P}-\text{F})$ | $l_g(\text{F} \cdots \text{F})$ | $l_g(\text{Pt} \cdots \text{F})$ | $l_g(\text{P} \cdots \text{P})$ | $l_g(\text{P} \cdots \text{F})$ | $R^b$ |
|--------------------------------------|--------------------------|--------------------------------------|---------------------------|--------------------------|---------------------------------|----------------------------------|---------------------------------|---------------------------------|-------|
| $r_g(\text{Pt}-\text{P})$            | -0.18                    | -0.81                                | -0.08                     | 0.27                     | 0.34                            | 0.16                             | 0.00                            | -0.05                           | 0.41  |
| $r_g(\text{P}-\text{F})$             | 1                        | -0.18                                | 0.00                      | -0.08                    | -0.11                           | -0.03                            | -0.02                           | -0.01                           | -0.11 |
| $\angle \text{Pt}-\text{P}-\text{F}$ |                          | 1                                    | -0.06                     | -0.38                    | -0.21                           | -0.15                            | -0.02                           | -0.15                           | -0.57 |
| $l_g(\text{Pt}-\text{P})$            |                          |                                      | 1                         | 0.26                     | -0.31                           | 0.03                             | 0.00                            | 0.14                            | 0.28  |
| $l_g(\text{P}-\text{F})$             |                          |                                      |                           | 1                        | 0.23                            | 0.14                             | 0.00                            | 0.22                            | 0.73  |
| $l_g(\text{F} \cdots \text{F})$      |                          |                                      |                           |                          | 1                               | 0.12                             | 0.00                            | -0.04                           | 0.33  |
| $l_g(\text{Pt} \cdots \text{F})$     |                          |                                      |                           |                          |                                 | 1                                | 0.26                            | -0.03                           | 0.20  |
| $l_g(\text{P} \cdots \text{P})$      |                          |                                      |                           |                          |                                 |                                  | 1                               | 0.24                            | 0.00  |
| $l_g(\text{P} \cdots \text{F})$      |                          |                                      |                           |                          |                                 |                                  |                                 | 1                               | 0.30  |
| $R^i$                                |                          |                                      |                           |                          |                                 |                                  |                                 |                                 | 1     |

<sup>a</sup>Matrix elements are given by  $\rho_{ij} = (M_x^w)_{ij} / [(M_x^w)_{ii}(M_x^w)_{jj}]^{1/2}$  where  $M_x^w$  is the bona fide error matrix.<sup>b</sup>Index of resolution.

reported the structure of Ni(PF<sub>3</sub>)<sub>4</sub> by gas-phase electron diffraction [6].  
Structure trends and implications were reviewed by these authors.

## ACKNOWLEDGEMENT

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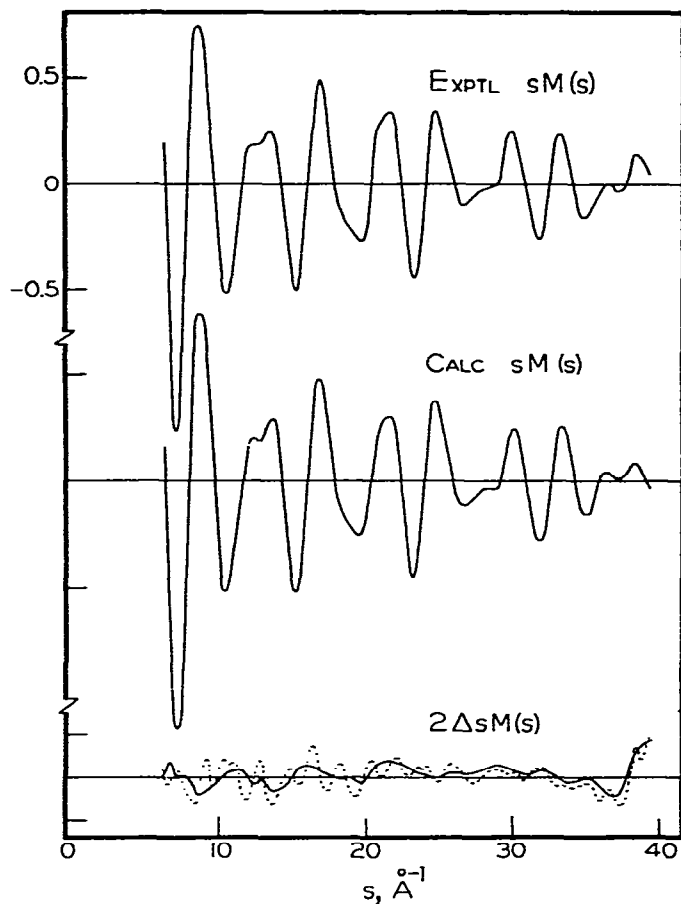


Fig. 1. Molecular intensity curves  $sM(s)$  for  $\text{Pt}(\text{Pf}_3)_3$  and residuals. Dashed residual curve, analysis not including dynamic corrections, solid curve, analysis including corrections.

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