4. von Auwers, K. *Ann.* **420** (1920) 84.
5. Skita, A. *Ber.* **56** (1923) 1014.
6. Eliel, E. L. *Stereochemistry of Carbon Compounds*, McGraw, New York 1962, p. 217.
7. Beineke, T. A. *Chem. Commun.* **1966** 860.
8. Geise, H. J. *Rec. Trav. Chim.* **86** (1967) 362.
9. Muragaa, W. and Kainosko, M. *To be published in Bull Chem. Soc. Japan.*

Received February 23, 1971.

Mean Amplitudes of Vibration for Tetrakis(trifluorophosphine)-nickel

S. J. CYVIN [a] and A. MÜLLER [b]

[a] *Institutt for teoretisk kjemi, Norges tekniske høgskole, N-7034 Trondheim, Norway and* [b] *Institut für Chemie, Universität Dortmund, West-Germany*

Tetrakis(trifluorophosphine)nickel, $Ni(PF_3)_4$, has recently been subjected to two independent gas electron diffraction works.[1,2] The results from these works agree well for the interatomic distances, but there is a controversy as regard to the P···P mean amplitude. Marriott *et al.*[1] have reported 0.2 – 0.3 Å in consistence with a rough estimate of 0.2 Å from spectroscopic data, while Almenningen *et al.*[2] have given $u(P\cdots P) = 0.101$ (0.016) Å. In the present work it is attempted to give a more accurate answer to this problem from elaborate spectroscopic calculations.

A diagonal force constant matrix in terms of symmetry coordinates [3] was chosen as the initial approximate form. After some preliminary calculations the following values of force constants were accepted as a starting point. Species A_1: 3.28, 8.08, and 0.86 mdyne/Å. A_2: 0.0294 mdyne/Å. E: 0.079, 4.164, 0.386, and 0.5 mdyne/Å. F_1: 4.50, 0.40, 0.40, and 0.0294 mdyne/Å. F_2: 2.27, 0.06, 5.25, 5.50, 0.55, 0.58, and 0.40 mdyne/Å. The calculated frequencies from this force field are shown in Table 1 along with available experimental data.[4–6]

The calculated mean amplitudes from the approximate force field are given as parenthesized figures in Table 2. The calculations were refined by adjusting the force constants to the frequency values shown in the last column of Table 1, where observed values have been used when available. The spectral data are seen to be rather incomplete, for which reason the final mean amplitudes (Table 2) must not be accepted without criticism. In particular the torsional frequencies of species A_2 and F_1 (lowest frequency) are very uncertain. The mean amplitudes which are substantially influenced by the values of these frequencies are marked in the table.

In spite of the large uncertainties of the present calculations the P···P mean amplitude seems to be fairly well established. Its value at room temperature appears to be in-between the two different estimates from electron diffraction, but the drastic dependence on temperature should be noticed. In general the electron

Table 1. Vibrational frequencies (cm^{-1}) for tetrakis(trifluorophosphine)nickel

Species	Raman (liquid) a	Raman (liquid) b	Infrared (gas) a	Infrared (gas) b	Calculated c	Calculated d
A_1	954	955	—	—	972	954
	534	534	—	—	518	534
	195	195	—	—	198	195
A_2	63?	—	—	—	63	63
E	851	—	—	—	865	851
	332	—	—	—	339	332
	—	—	—	—	301	301
	54	—	—	—	54	54
F_1	—	—	—	—	890	890
	—	—	—	—	349	349
	—	—	—	—	271	271
	—	—	—	—	37	37
F_2	883	892	898	894	968	898
	883	850	860	857	809	860
	505	501	508	—	528	508
	385	383	390	—	403	390
	—	—	287?	—	261	287
	219	218	217	—	216	217
	54	50	52	—	52	52

a. Refs. 3 and 4.
b. Ref. 5.
c. From initial approximate force field.
d. From final force field.

Table 2. Mean amplitudes of vibration (Å units) for tetrakis(trifluorophosphine)nickel.

Distance type [a]	R [b]	u approx. 298°K	u final 0°K	u final 298°K	E.D.[e]	Approx.[f] 298°K
P —F	1.561	(0.042)	0.041	0.042	0.034	(0.040)
Ni—P	2.099	(0.048)	0.040	0.047	0.049	(0.071)
P ···P	3.428	(0.142)	0.065	0.142	0.101	
Ni···F	3.004	(0.080)	0.059	0.079	0.093	(0.084)
P ···F	3.766 [c]	(0.236)	0.095 [d]	0.236 [d]		
P ···F	4.788 [c]	(0.119)	0.067	0.119	0.086	
F ···F	2.549	(0.071)	0.061	0.071	0.072	(0.069)
F ···F	3.428 [c]	(0.369)	0.137 [d]	0.371 [d]		
F ···F	4.272 [c]	(0.333)	0.124 [d]	0.334 [d]	0.65	
F ···F	5.195 [c]	(0.229)	0.097 [d]	0.230 [d]		
F ···F	5.977 [c]	(0.100)	0.073	0.100		

[a] Same sequence as in Ref. 3.
[b] Interatomic distances from the structural data adopted here. All angles were assumed as tetrahedral.
[c] Angle-dependent distances with respect to internal rotation.
[d] Uncertain because of influence from unknown torsional frequencies.
[e] Electron diffraction data from Ref. 2.
[f] For the $NiPF_3$ fragment according to the method of characteristic vibrations using measured bond angles.[1,2]

diffraction data [2] of mean amplitudes for the angle-independent distances agree satisfactorily with the present calculations.

Approximate mean amplitudes were also calculated tentatively for the two fragments $NiPF_3$ (C_{3v}) and $Ni(PF_3)_2$ (XY_2-pseudomolecule) according to the method of characteristic vibrations. (In the case of $NiPF_3$ this is a modification of the principles in Ref. 7, because the whole fragment was taken into consideration.) In the first case the developed force constants F_{ij} ($i \leq j$) are as given in the following (in mdyne/Å; diagonal elements in italics; based on previously reported symmetry coordinates[8]). A_1: *6.50*, 0.10, 0.12, *0.92*, −0.05, *0.52*; E: *5.47*, −0.04, 0.05, *0.53*, 0.00_3, *0.34*. They are consistent with the average frequency values of (A_1) 933, 519, and 207 cm^{-1}, and (E) 931, 359, and 287 cm^{-1}. From these calculations (see Table 2) three of the u-values agree very well with the rigorous calculations. The large discrepancy for u(Ni−P) is supposed to be mainly due to differing Ni−P stretching force constants (compare for instance 0.92 in the fragment with 3.28 mdyne/Å in the whole molecule). In the latter case using $Ni(PF_3)_2$ one cannot expect good results because the mass of (PF_3) is larger than the mass of Ni.[7,9] With plausible average frequencies $u(P\cdots P) \approx 0.19$ Å was obtained, which is close to the approximate estimate in Ref. 1.

1. Marriott, J. C., Salthouse, J. A., Ware, M. J. and Freeman, J. M. *Chem. Commun.* **1970** 595.
2. Almenningen, A., Andersen, B. and Astrup, E. E. *Acta Chem. Scand.* **24** (1970) 1579.
3. Cyvin, S. J. *To be published.*
4. Woodward, L. A. and Hall, J. R. *Spectrochim. Acta* **16** (1960) 654.
5. Edwards, H. G. M. and Woodward, L. A. *Spectrochim. Acta* **A 26** (1970) 897.
6. Loutellier, A. and Bigorgne, M. *J. Chim. Phys.* **67** (1970) 78, 99, 107.
7. Müller, A., Peacock, C. J., Schulze, H. and Heidborn, U. *J. Mol. Struct.* **3** (1969) 252.
8. Müller, A., Krebs, B., Fadini, A., Glemser, O., Cyvin, S. J., Brunvoll, J., Cyvin, B. N., Elvebredd, I., Hagen, G. and Vizi, B, *Z. Naturforsch.* **23a** (1968) 1656.
9. Baran, E. J. *Z. Naturforsch.* **25a** (1970) 1292.

Received February 3, 1971.