Harmonic Force Field and Mean Amplitudes for C_4Cl_4 and C_4F_4 Compounds

G. Díaz

Departamento de Química, Universidad de Chile, Valparaíso, Chile

Z. Naturforsch. **37 a**, 1292–1294 (1982); received April 28, 1982*

Normal coordinate treatment of C_4F_4 and C_4Cl_4 in the GVFF was performed using published vibrational frequencies. The vibrational assignment for these molecules is discussed. Calculated mean amplitudes for both molecules are reported.

Introduction

Relatively few works have been published concerning molecules with 3 cumulated double bonds. Butatriene C_4H_4, which is the simplest known molecule of this type, other than carbon suboxide and carbon subsulphide has been extensively studied. The rotational Raman spectrum was measured by Stoicheff [1], and in an electron diffraction study Almenningen et al. [2] give the bond distances based on a planar model. The complete Raman and IR spectra of butatriene based on D_{2h} point group were analyzed by Miller and Matsubara [3]. Mean amplitudes of vibration have also been reported for C_4H_4 [4–6]. Moreover a vibrational analysis of tetramethyl butatriene has been carried out by Rogstad [7].

In a recent study the vibrational spectra of perfluorobutatriene C_4F_4 and perchlorobutatriene C_4Cl_4 [8] were recorded with the aim of determining the symmetry of the molecules and to obtain a better understanding of compounds with skeletons of cumulated double bonds. However, no work on the normal coordinate analysis of these molecules has been done so far. Hence a vibrational analysis for the planar normal modes of C_4F_4 and C_4Cl_4 giving rise to the force constants and mean amplitudes of vibration has been carried out in the present investigation.

Molecular Model

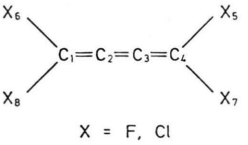
Similar to the butatriene molecule, C_4F_4 and C_4Cl_4 have D_{2h} symmetry, and their fundamental frequencies span the following irreducible representations: $4A_{1g} + 3B_{1u} + 3B_{3g} + 3B_{2u} + A_u + 2B_{2g} + 2B_{3u}$. The nine vibrations belonging to $4A_{1g}$, $2B_{2g}$ and $3B_{3g}$ are Raman active and the remaining are IR active. The A_u vibration is tentatively suggested to be due to torsion. The geometry of the molecules is shown in Fig. 1, where the x-axis is taken perpendicular to the plane of the molecule and the z-axis along the C – C line, as recommended by the Joint Commission for Spectroscopy [9]. The orthonormal set of symmetry coordinates used in this investigation is similar to that given by Cyvin et al. [10] for C_4H_4.

Molecular Force Fields and Vibrational Assignments

In order to solve the equation [11] $FGL = L\Lambda$ for C_4F_4 and C_4Cl_4, the G matrix was constructed after assuming C = C distance = 1.28 Å, outer C = C distance = 1.32 Å, C – F = 1.32 Å, C – Cl = 1.72 Å and XCX angle 110° (X = F, Cl). These dimensiones were chosen by analogy with butatriene [2], 1.1-difluoroallene [12] and perchloroethylene [13].

A very simple force field approximation was chosen to calculate a set of initial vibrational frequencies. It is represented by a diagonal force constant matrix in terms of the valence coordinates. The numerical values of these constants are collected in Table 1, showing the regularities through the series of molecules in question.

The diagonal force constant matrix was converted to F matrix blocks in terms of symmetry



X = F, Cl

Fig. 1. Molecular model of perhalo-butatriene.

* The first version was received on February 10, 1982.

Reprint requests to Prof. G. Díaz, Universidad de Chile, Casilla 130-V, Valparaíso, Chile.

0340-4811 / 82 / 1100-1292 $ 01.30/0. — Please order a reprint rather than making your own copy.

Table 1. Force constants (mdyn/Å) of approximate force fields for C_4F_4 and C_4Cl_4.

Symbol	C_4F_4	C_4Cl_4
f_{C-X}	6.00	5.00
f_{C-C}	10.00	10.00
$f_{X_2\,bend.}$	2.40	1.50
$f_{CX_2\,rock.}$	0.20	0.15
$f_{CCC\,bend.}$	0.18	0.13

coordinates and the corresponding vibrational frequencies were computed. The approximate calculated frequencies for C_4F_4 and C_4Cl_4 are shown in Table 2.

The approximate force fields may be used to discuss the experimental assignments of frequencies since it is supposed that they reproduce their general features, although a quantitative agreement with the observed fundamentals cannot be expected.

At this respect, the calculations basically confirm the straightforward experimental assignments of Miller et al. [8]. In the case of those assignments pointed out as doubtful by these authors, the calculated frequencies in the A_{1g} species of C_4F_4 favour the adoption of the band at 1373 cm^{-1} as the second chain mode. This frequency was discarded by Miller et al. [8], although they also considered this band as a possibility for the current assignment. For the B_{1u} CCl_2 symmetric stretching, the band at 610 cm^{-1} is in better agreement with the calculated frequency (624 cm^{-1}) than the band at 870 cm^{-1} tentatively assigned to this normal mode by Miller et al. [8].

Table 2. Calculated and observed vibrational frequencies (cm^{-1}) for C_4F_4 and C_4Cl_4.

Species	C_4F_4		C_4Cl_4	
	Approx.	Final[a]	Approx.	Final[a]
A_{1g}	2356	2140	2226	2071
	1408	1373	1222	1112
	669	681	412	416
	359	353	216	194
B_{1u}	1785	1738	1657	1612
	896	943	624	610
	542	539	296	294
B_{3g}	1277	1255	902	981
	407	476	324	321
	180	185	127	138
B_{2u}	1268	1278	1056	890
	538	569	389	341
	191	(178)	105	(124)

[a] Calculated from the final force fields and identical to the experimental data from [8]. Parenthesized values are unobserved.

For the B_{2u} and B_{3g} rocking modes of C_4F_4 and C_4Cl_4, the results of this work seem to confirm the conjecture of Miller et al. [8] in relation to the abnormally high values of the frequencies which they have assigned to these vibrations. In the B_{2g} species the calculated bands at 538 cm^{-1} for C_4F_4 and 389 cm^{-1} for C_4Cl_4 can be compared with those assigned by Miller et al. [8] to in-plane skeletal bending modes of these molecules, while in the B_{3g} species the corresponding computed values at 407 cm^{-1} and 324 cm^{-1} resemble those proposed in the previous work as the wagging modes of C_4F_4 and C_4Cl_4, respectively.

On the other hand, the calculated frequencies for the in-plane skeletal bending modes in the B_{3g} and B_{2u} species of C_4F_4 and C_4Cl_4, appear to be much lower than the values assigned by Miller et al. [8] to these normal modes. The calculated bands for the B_{3g} species of these vibrations, 180 cm^{-1} for C_4F_4 and 127 cm^{-1} for C_4Cl_4, are comparable to those ascribed in [8] to B_{2g} out-of-plane skeletal bending modes of the molecules here considered.

The initial force fields for C_4F_4 and C_4Cl_4 were adjusted by a simple minimizing method [14] to fit exactly the observed frequencies of the alternative assignation described above (see Table 2). The final symmetry force fields for the planar vibrations of these molecules are shown in Tables 3 and 4.

The values of the final symmetry force constants concerning the C=C stretching modes for C_4F_4, $F_{22}(A_{1g})$, $F_{33}(A_{1g}$ and $F_{22}(B_{1u})$, are higher than those obtained for C_4Cl_4. A similar trend for C_2F_4 and C_2Cl_4 has been pointed out by Ramaswamy et al. [15].

Table 3. Final symmetry force constants (mdyn/Å) for C_4F_4.

	A_{1g}	6.096	1.239	0.776	−0.068		
			10.586	1.283	−0.302		
				11.560	−0.494		
					2.420		
B_{1u}	6.102	1.176	−0.179	B_{3g}	5.794	0.151	0.001
		9.648	−0.219			0.203	−0.003
			2.335				0.240
	B_{2u}	5.053	0.145	0.057			
			0.192	0.010			
				0.231			

Table 4. Final symmetry force constants (mdyn/Å) for C_4Cl_4.

	A_{1g}	4.667	0.646	0.452	−0.066		
			9.065	0.298	−0.049		
				8.991	−0.091		
					1.312		
B_{1u}	3.906	0.516	0.212	B_{3g}	3.050	0.006	0.003
		8.445	0.160			0.120	0.002
			1.315				0.153
	B_{2u}	3.056	0.083	0.000			
			0.102	0.003			
				0.101			

Mean Amplitudes of Vibration

The final force fields were used to calculate the mean amplitudes of vibration (l) for both molecules, according to well-established methods [16]. The results at the temperatures of absolute zero and 298 K for C_4F_4 and C_4Cl_4 are given in Tables 5 and 6, respectively.

Although no experimental data are available for comparison, the present calculated C − X (X = F, Cl) mean amplitudes of vibration seem to have reasonable values which are considered characteristic for a large number of polyatomic molecules, as summarized by Müller et al. [17]. The l (C = C) values are in agreement with those obtained through an empirical relation established from statistical treatment of 57 electron diffraction measurements by Cyvin et al. [18].

Table 5. Mean amplitudes of vibration (in Å) for C_4F_4 at 0 K and 298 K.

Distance Type	(Equil. dist./A)	Mean amplitudes	
		$T = 0$	298 K
$C_1 - C_2$	(1.320)	0.039	0.040
$C_1 \ldots C_3$	(2.600)	0.045	0.046
$C_1 \ldots C_4$	(3.880)	0.048	0.050
$C_2 - C_3$	(1.280)	0.038	0.039
C − F	(1.320)	0.044	0.044
$C_2 \ldots F_5$	(3.520)	0.063	0.070
$F_5 \ldots F_7$	(2.162)	0.054	0.058
$C_3 \ldots F_5$	(2.340)	0.053	0.060
$C_1 \ldots F_5$	(4.791)	0.065	0.080
$F_5 \ldots F_6$	(5.420)	0.085	0.112

Table 6. Mean amplitudes of vibration (in Å) for C_4Cl_4 at 0 K and 298 K.

Distance Type	(Equil. dist./A)	Mean amplitudes	
		$T = 0$	298 K
$C_1 - C_2$	(1.320)	0.041	0.041
$C_1 \ldots C_3$	(2.600)	0.047	0.049
$C_1 \ldots C_4$	(3.880)	0.051	0.054
$C_2 \ldots C_3$	(1.280)	0.040	0.041
C − Cl	(1.720)	0.046	0.048
$C_2 \ldots Cl_5$	(3.853)	0.063	0.070
$Cl_5 \ldots Cl_7$	(2.817)	0.053	0.060
$C_3 \ldots Cl_5$	(2.703)	0.054	0.062
$C_1 \ldots Cl_5$	(5.105)	0.068	0.081
$Cl_5 \ldots Cl_6$	(5.893)	0.087	0.121

Acknowledgement

The author wishes to express his indebtedness to Professor Foil A. Miller at University of Pittsburgh for his encouragement and valuable advice. Thanks are also due to "Departamento de Química, Universidad Católica de Valparaíso" for permission to use the IBM 370 computer.

[1] B. P. Stoicheff, Can. J. Phys. **35**, 837 (1957).
[2] A. Almenningen, O. Bastiansen, and M. Traetteberg, Acta Chem. Scand. **15**, 1557 (1961).
[3] F. A. Miller and I. Matsubara, Spectrochim. Acta **22**, 173 (1966).
[4] K. Ramaswamy and K. Srinivasan, J. Mol. Struct. **3**, 473 (1969).
[5] K. Venkateswarlu, K. V. Rajalakshmi, and A. Natarajan, Bull. Soc. Roy. Sci. Liège **36**, 347 (1967).
[6] S. J. Cyvin and G. Hagen, Acta Chem. Scand. **23**, 2037 (1969).
[7] A. Rogstad, Spectrochim. Acta **36A**, 131 (1980).
[8] F. A. Miller, W. F. Elbert, and W. Pingitore, J. Mol. Struct. **40**, 25 (1977).
[9] Joint Commission for Spectroscopy, J. Chem. Phys. **23**, 1997 (1955).
[10] S. J. Cyvin, P. Klaeboe, and E. Aughdal, Acta Chem. Scand. **19**, 833 (1965).
[11] E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.
[12] J. R. Durig, Y. S. Li, C. C. Tong, A. P. Zens, and P. D. Ellis, J. Amer. Chem. Soc. **96**, 3805 (1974).
[13] L. Karle and J. Karle, J. Chem. Phys. **20**, 63 (1952).
[14] P. Nectoux and R. Rousson, J. Mol. Spectr. **59**, 1 (1976).
[15] K. Ramaswamy and P. Ramanathan, J. Mol. Struct. **51**, 127 (1979).
[16] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Elsevier, Amsterdam, Universitetsforlaget, Oslo 1968.
[17] A. Müller, E. J. Baran, and K. H. Schmidt, in Molecular Structure and Vibrations (S. J. Cyvin Ed.), Elsevier, p. 376–391, 1972, Chapter 21.
[18] S. J. Cyvin and V. S. Mastryukov, J. Mol. Struct. **30**, 333 (1976).