On Centrifugal Distortion and Urey-Bradley Force Field of Chlorofluoromethane

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A normal coordinate treatment of chlorofluoromethane has been performed in the Urey-Bradley force field model using the centrifugal distortion constants and the vibrational frequencies. Since the molecule has only one plane of symmetry (C_s), the symmetrized internal coordinates have not been used in the calculation. The effect of the angular redundancy has been rigorously treated and the derived force constants are in good agreement with those of other halogenated methane.

The molecule chlorofluoromethane (CH_2ClF) is an asymmetric-top molecule having one plane of symmetry and the two hydrogen atoms are symmetrically disposed above and below the plane ($H(+)$ and $H(-)$). In an earlier publication, El-Sabban et al. [1] have calculated the force constants of this molecule in the general valence force field. In their calculation, the intramolecular tension k has been tentatively assumed. Moreover, this molecule has only nine vibrational frequencies and the number of independent force constants in the general valence force field is thirty four. As a result, the force constants reported in Ref. [1] cannot be regarded as unique. This suggests that we undertake the calculation in the model force field, which in this case is the Urey-Bradley force field. The number of unknown force constants necessary to define the potential energy in the UBFF model is twelve, namely, K_{C-F}, K_{C-Cl}, K_{C-H}, F_{F-Cl}, F_{F-H}, F_{Cl-H}, F_{H-H}, k, H_{F-Cl}, H_{F-H}, H_{Cl-H} and H_{H-H}. K, H, F and k denote, respectively, the stretching, bending, repulsive and intramolecular tension. The unique evaluation of twelve force constants requires at least three more observables besides the nine observed vibrational frequencies. The analysis of the microwave spectrum of chlorofluoromethane by Nandi and Chatterji [2] provides a set of five centrifugal distortion constants d_J, d_{JK}, d_K, d_{WJ} and d_{WK} [3]. These centrifugal distortion constants are some linear combinations of Kivelson's parameters τ_{aaaa}, τ_{bbbb}, τ_{cccc}, τ'_{aabb} etc. [4]. From the five observed quartic centrifugal stretching constants, we have evaluated three principal Kivelson's parameters τ_{aaaa}, τ_{bbbb} and τ_{cccc}. Using these three principal centrifugal distortion constants as additional data along with nine vibrational frequencies [5], the twelve force constants of the U.B. force field are calculated uniquely.

In CH_2ClF, there are four bond lengths and six bond angles giving in all ten internal coordinates. However all the bond angles are not independent and there is a redundancy among the six bond angles. The effect of this angular redundancy is two fold, firstly the internal coordinate force constants f_{ij} are modified and secondly, the perturbation technique for the evaluation of force constants as suggested by Mills [6], Overend and Scherer [7] cannot be applied unless all the coordinates are independent and the F and G matrices are evaluated in the independent set of coordinates. The angular redundancy has been treated following the method of Crawford and Overend [8], Godnev and Orlova [9].

According to Ref. [8, 9], one can declare any of the six bond angles to be redundant and in our case we declare the angle $\Delta\alpha_{F-C-H(-)}$ as the same one and will use the following set of internal coordinates which are independent, namely, Δr_{C-Cl}, Δr_{C-F}, $\Delta r_{C-H(+)}$, $\Delta r_{C-H(-)}$, $\Delta\alpha_{F-C-Cl}$, $\Delta\alpha_{F-C-H(+)}$, $\Delta\alpha_{Cl-C-H(+)}$, $\Delta\alpha_{H(+)-C-H(-)}$ and $\Delta\alpha_{Cl-C-H(-)}$. The set of dependent internal coordinates S is related to the set of independent coordinates S' by the following matrix equation

$$S = M S' . \tag{1}$$

The elements of the force constant matrix F are suitably modified due to the contribution from the second order redundancy relation. The matrix F in the dependent set of coordinates is related to the force constant matrix F_0 in the independent set of coordinates by the following equation

$$F_0 = M' F M \tag{2}$$

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where M' is the transpose of M [8]. The elements of F_0 are then expressed in terms of U.B. parameters and can be conveniently employed in the iterative perturbation calculation [6, 7]. The G-matrix in the independent set of coordinates is obtained simply by deleting the row and the column corresponding to the redundant coordinate [10]. The centrifugal distortion constant is related to the molecular force field through the following equation

$$\tau_{\alpha\beta\gamma\delta} = \frac{-1}{2\, I_{\alpha\alpha} I_{\beta\beta} I_{\gamma\gamma} I_{\delta\delta}} \sum_{i,j=1}^{n} J_{\alpha\beta}^{(i)} J_{\gamma\delta}^{(j)} (F^{-1})_{ij} \quad (3)$$

where $I_{\alpha\alpha}$, $I_{\beta\beta}$ etc. are the principal moments of inertia and $J_{\alpha\beta}$, $J_{\gamma\delta}$ etc. are the derivatives of the moments of inertia. The latter quantities have been evaluated following the method of Pulay and Sawodny [11].

The principal moments of inertia and the molecular geometry are taken from Ref. [2]. F_0, G matrix and the derivatives of the moments of inertia are not reported in this paper and are available from the authors on request. In the perturbation calculation, nine vibrational frequencies along with three principal distortion constants τ_{aaaa}, τ_{bbbb} and τ_{cccc} of ^{35}Cl species have been used. The necessary Jacobian for vibrational frequency and centrifugal distortion constant has been evaluated following the method of Mills [6]. In this calculation we have assigned unit weight to all the observables.

The observed and the calculated frequencies together with τ_{aaaa}, τ_{bbbb} and τ_{cccc} are given in Table 1. We have also calculated the five quartic centrifugal distortion constants of Watson namely d_J, d_{JK}, d_K, d_{WJ} and d_{WK}. They have been compared with the observed values and the agreement is good. The UBFF parameters as obtained from this calculation are given in Table 2. These force constants are compared with those obtained from other halogenated methane e.g. CH_3X [12] and CHX_3 [13, 14]. They compare quite favourably and the small difference is due to the change in chemical environment of the various molecules in question.

Table 1. The observed and the calculated values of frequencies (in cm^{-1}) and centrifugal distortion constants (in MHz) of $CH_2{}^{35}ClF$.

	Observed	Calculated	Difference (Obs.-Cal.)
ν_1	3048	3057	− 9
ν_2	2993	2983	10
ν_3	1468	1468	0
ν_4	1351	1375	−24
ν_5	1236	1245	− 9
ν_6	1068	1067	1
ν_7	1000	977	23
ν_8	760	759	1
ν_9	385	386	− 1
τ_{aaaa}	−2.0358	−2.037	0.002
τ_{bbbb}	−0.02003	−0.01841	−0.00162
τ_{cccc}	−0.011494	−0.01029	−0.001204
d_J [a]	-1.84011×10^{-2}	-1.76659×10^{-2}	
d_{JK}	−0.734316	−0.756631	
d_K	−3.17095	−3.34417	
d_{WJ}	4.1×10^{-6}	3.89578×10^{-6}	
d_{WK}	1.019×10^{-4}	1.06784×10^{-4}	

[a] Watson's parameters were not included in the analysis but τ_{aaaa}, τ_{bbbb} and τ_{cccc} were included.

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Table 2. Urey-Bradley force constants of CH_2ClF. The angle α_{ij} for CH_2ClF is scaled with $(r_i r_j)^{1/2}$ and all force constants are millidyne/Å.

	K_{C-F}	K_{C-Cl}	K_{C-H}	F_{F-Cl}	F_{F-H}	F_{Cl-H}	F_{H-H}	k	H_{F-Cl}	H_{F-H}	H_{Cl-H}	H_{H-H}
CH_2ClF	3.87	1.742	4.069	0.773	1.111	0.955	−0.083	−0.139	0.150	0.11	0.025	0.40
$CHCl_3$ [14]		1.804	4.226			0.768		0.169			−0.003	
CHF_3 [13]	4.331		3.445		1.158			0.371		−0.009		
CH_3F [12]	3.36		4.63		1.21		0.09	0.17		0.110		0.42
CH_3Cl [12]		1.60	4.89			0.93	0.15	0.11			0.02	0.40

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