PARAMETER STUDY OF FORCE FIELDS OF SOME TETRAHEDRAL MOLECULES AND IONS

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The parameter method for determinating the exact force field is applied to some XY_4 type molecules and ions. In those cases where a unique force field cannot be determined, methods for arriving at an acceptable force field are outlined.

Force constants for XY_4 type molecules and ions with T_d symmetry have been evaluated by many workers, following different approaches [1–13]. In most of these works the force constants of the two dimensional F_2 species are fixed from vibrational frequencies using additional experimental data such as isotopic frequencies, Coriolis constants and centrifugal distortion constants or applying some approximation method. Recently Ananthakrishnan et al. [14] have discussed the problem of determination of force constants using isotopic frequencies in the parameter formalism in which each force constant F_{ij} in a second order vibrational problem is expressed as a function of a parameter c. The parameter $(c-c^*)$ curves for each pair of isotopic species are plotted and intersections are sought [14]. If isotopic invariance is to hold, there should exists a unique point of intersection of all three parametr curves and the force constants corresponding to this point must be the same for all the isotopic substituents. However, in many cases unique intersections of parameter curves do not exist because of inaccuracies in experimental data. When the curves intersect forming small islands, the force constants have been evaluated as the mean of the values corresponding to the extreme points of the island [14]. When the number of isotopic species exceeds two, there will be a multiplicity of intersections. In such cases, we have recently applied a principle called the method of equal coordinates [15] which may be stated as follows: If A, B, C are isotopic species of the same molecule, the intersections of parameter curves for the pairs A–B and B–C should be such that B is represented by equal coordinates in the parameter spaces $c_A - c_B$ and $c_B - c_C$. According to this approach intersections are sought from parameter curves plotted in separate two dimensional spaces, considering one pair at a time.

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When we consider three or more isotopic species, there exist a number of intersections near the origin. But these intersections lie in a small region in the given parameter space. As the parameter for the true force field should lie inside this range, the size of this region may be taken as a measure of the uncertainty in fixing true coordinate. With the help of more than two parameter spaces the extent of uncertainty can be reduced. The minimum value of the uncertainty obtained from an analysis of the graphs corresponds

TABLE I

Force constants of some XY_4 type molecules and ions

Molecule or ion	Force constants in mdyn/A		
	Present result	Previous result	
CF_4	F_{11} 6.4559 F_{12} −0.8208 F_{22} 1.0115	6.489 6.22±0.25 −0.827 [8] −0.84 [4] 1.010 1.01	
XeO_4	F_{11} 6.3701±0.0453 F_{12} 0.2379±0.0516 F_{22} 0.3722±0.0065	6.480 0.110 [11] 0.359	
SiF_4	F_{11} 6.3388 F_{12} −0.2593 F_{22} 0.4396	6.36 6.201 −0.269 [6] −0.194 [7] 0.439 0.445	
SiH_4	F_{11} 3.0305 F_{12} −0.0163 F_{22} 0.2401	3.032 −0.025 [4] 0.240	
BF_4	F_{11} 4.7915 F_{12} −0.9933±0.0050 F_{22} 0.6454	3.88 5.094 −0.53 [9] −0.8712 [2] 0.72 0.699	
NH_4	F_{11} 6.0224 F_{12} −0.0667 F_{22} 0.5599		

to the smallest range common to all the parameter spaces. The common range thus selected must also satisfy the equal coordinates criterion. The mean of the force constant values for the extreme points of the common range along with the extent of the uncertainties is taken as the true force constant. All points of intersection, whether unique or not, outside the corresponding common range are taken as spurious ones and are automatically eliminated. This method has been applied to the following molecules and ions: $^{12}CF_4$, $^{13}CF_4$, $Xe^{16}O_4$, $Xe^{18}O_4$, $^{28}SiF_4$, $^{29}SiF_4$, $^{30}SiF_4$, SiH_4, SiD_4, SiT_4, $^{10}BF_4$, $^{11}BF_4$, NH_4, $^{15}NH_4$, ND_4, NT_4. The results are entered in Table I and compared with values taken from the literature. Vibrational frequencies are taken from Refs [3, 4, 6, 8, 11, 16, 17]. Symmetry coordinates and G matrix elements used here are those reported by Cyvin [17].

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