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Force constants from intensity analysis of molecules CH_3Cl and CD_3Cl

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Abstract. The secular equation $(GF - E\lambda)L = 0$ contains more force constants than can be calculated from the equations formulated using the frequencies. For a 3×3 matrix, there are 6 force constants but only 3 frequencies. Attempts were made by others to estimate all the 6 constants to satisfy the frequencies and Coriolis constants and rotation distortion constants. However, many attempts are not made in these estimations to satisfy the intensities. A full complement of equations is derived to evaluate all the force constants combining the intensity equations $I = L'A$ with $LL' = G$ and evaluated the force constants of A_1 species of CH_3Cl and CD_3Cl. A simple analysis of a 2×2 matrix shows that $F_{12}/F_{22} = G_{12}^{-1}/G_{22}^{-1}$ as reported earlier.

Keywords. Force constants; intensity analysis; methyl chlorides.

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1. Introduction

It is well known that the secular equation $(GF - E\lambda)L = 0$ contains more force constants than can be calculated from the number of equations available. A 3×3 matrix contains 6 force constants and only 3 equations corresponding to the three frequencies $\lambda(= 4\pi^2\sigma^2c^2)$ that can be formulated. Many attempts have been made over the years to arrive at all the 6 constants by making a number of approximations. These centre round determining L elements from

$$LL' = G \tag{1}$$

and substituting them in

$$L'FL = \Omega \tag{2}$$

Ω is a diagonal matrix of λ's. L' is transpose of L which connects symmetry coordinates and normal coordinates. But, L is an unsymmetrical matrix containing 9 elements, and G is symmetrical containing 6 elements and hence are not sufficient to determine all the F elements. Many of the approximations are made on the L elements. For instance, Torkington (1949) assumed that all the non-diagonal L elements can be neglected. Thirugnanasambandam and Karunanidhi (1976) published a number of papers extending over a large number of molecules, using an approximation $F_{ij}/F_{jj} = K_{ij}/K_{jj}$. K's are kinetic constants. They also, incorporated the idea of reflex angles suggested by Ford and Orville Thomas (1967) and adjusted the symmetric force constants. Combining these equations and frequencies, all the force constants