FORCE FIELD CALCULATIONS FROM INFRARED INTENSITIES AND ZETA CONSTANTS (FOR *E* SPECIES OF CH_3Cl, CH_3Br, CH_3I MOLECULES)

V. DAYANAND and K. RAVINDRANATH
Department of Physics, Osmania University, Hyderabad 500 007, India.

ABSTRACT

Infrared intensities of *E* modes of CH_3X (X = Cl, Br, I) are used along with zeta constants in the computation of accurate force fields of these molecules.

INTRODUCTION

RECENTLY[1] we presented a method for the calculation of force fields from Raman and infrared intensities for 2 × 2 species for CH_4, CD_4, CT_4. We now present a method of calculation of force fields for *E* species (3 × 3) of CH_3X (X = Cl, Br, I) with the help of infrared intensities and zeta constants. Earlier papers published from this laboratory involved approximation about the value of certain *L* elements[2] which was used for the calculation of force constants. In the present method, the calculation of force constants is made without making any approximation about any *L* matrix elements.

The relationships between intensities, electro-optical parameters and geometry of the molecule are:

$$I = L' A, \tag{1}$$
$$LL' = G. \tag{2}$$

Equation 1 gives three equations connecting intensities, electro-optical parameters and *L* elements. Equation (2) gives six equations relating *L* elements (which connect symmetry coordinates and normal coordinates) and *G* elements for the 3 × 3 species. The intensities and electro-optical parameters are taken from references 3 and 4.

Determination of L^{-1} elements

There are nine equations and nine unknown L^{-1} elements, but these equations are non-homogeneous and are not independent. Hence they cannot be solved absolutely. The equations connecting L_{64}^{-1}, L_{65}^{-1} and L_{66}^{-1} are as follows:

$$K_{11} L_{65}^{-1} = K_{12} L_{64}^{-1} + l_2 I_6 \pm (l_{12}^2 \Delta_4)^{\frac{1}{2}}, \tag{3}$$
$$K_{11} L_{66}^{-1} = K_{13} L_{64}^{-1} + l_4 I_6 + (l_{13}^2 \Delta_4)^{\frac{1}{2}}, \tag{4}$$

where K_{ij}'s, l_i's, l_{ij}^2's are constants and are dependent on intensities, electro-optical parameters and *G* elements. An equation connecting L_{65}^{-1} and L_{66}^{-1} can also be written similarly.

When the values of L_{64}^{-1}, L_{65}^{-1} and L_{66}^{-1} are determined, the other L^{-1} elements are calculated using the formulae.

$$I_{45}^2 L_{44}^{-1} = A_4' I_4 \pm (I_5^2 \Delta_4)^{\frac{1}{2}}, \tag{5}$$
$$I_{45}^2 L_{54}^{-1} = A_4' I_5 \pm (I_4^2 \Delta_4)^{\frac{1}{2}}, \tag{6}$$

where

$$I_{45}^2 = I_4^2 + I_5^2, \tag{7}$$

and

$$\Delta_4 = (G_{44}^{-1} - L_{64}^{-1^2}) I_{45}^2 - A_4'^2, \tag{8}$$

and

$$A_4' = A_4 - L_{64}^{-1} I_6, \tag{9}$$

similar equations can be written connecting

L_{45}^{-1}, L_{55}^{-1} with L_{65}^{-1} and L_{46}^{-1}, L_{56}^{-1} with L_{66}^{-1}.

For a single value of L_{64}^{-1}, we get two values of L_{65}^{-1} and six values of L_{66}^{-1}. Two values of L_{66}^{-1} are obtained from L_{64}^{-1} from (5) and four values of L_{66}^{-1} from the two values of L_{65}^{-1}. A computer program was made to calculate L_{65}^{-1} and L_{66}^{-1} for a given range of L_{64}^{-1}. The result in the case of CH_3Cl (*E* species) for $L_{64}^{-1} = -0.2362$ are given below.

$$L_{64}^{-1} = -0.2362$$

Values of L_{65}^{-1} (from equation 4)

0.5716 . . . 0.3210

Values of L_{66}^{-1} from L_{64}^{-1} (from equation 5)

0.8266 . . . −1.3658

Values of L_{66}^{-1} from the value of $L_{65}^{-1} = 0.5716$

0.8266 . . . −1.2150

Value of L_{66}^{-1} from the value of $L_{65}^{-1} = 0.3210$

1.0400 . . . −1.3658.

Equal values of L_{66}^{-1} obtained from L_{64}^{-1} and L_{65}^{-1} will be taken up for further determination of L^{-1} elements. From the above results we can write L_{64}^{-1}, L_{65}^{-1} and L_{66}^{-1} in two sets.

Table 1 *Values of L_{6i}^{-1} elements*

$L_{64}^{-1} = -0.2362$	$L_{65}^{-1} = 0.5716$	$L_{66}^{-1} = 0.8266$
$L_{64}^{-1} = -0.2362$	$L_{65}^{-1} = 0.3210$	$L_{66}^{-1} = -1.3658$

From the above table we conclude that for every value of L_{64}^{-1}, we get two sets of L^{-1} matrices, which satisfy (1) and (2) in their inverse form, hence we get an infinite sets of L^{-1} matrices as the value of L_{64}^{-1} is allowed to take any random value.

Utility of Zeta 66 element

To over-come the above difficulty we have used Zeta 66 matrix value to fix the last row of the L^{-1} matrix. We know that[5].

$$L^{-1} G L^{-1'} = E \tag{10}$$

and

$$L^{-1} (G - C) L^{-1'} = E - \text{Zeta}. \tag{11}$$

In (11) C is a matrix similar to the G matrix which depends on masses and interatomic distances of the molecule and is called as compliance constant matrix. From the above two equations the following equation is derived:

$$L_{64}^{-1^2} - \frac{2(2)^{\frac{1}{2}}}{d} L_{64}^{-1} L_{65}^{-1} + \frac{3}{d^2} L_{65}^{-1^2} + \frac{2}{d^2} L_{65}^{-1} L_{66}^{-1} + \frac{L_{66}^{-1^2}}{d^2} = \frac{1 - \text{Zeta } 66}{u_H}, \tag{12}$$

where u_H is the inverse mass of the hydrogen atom and d is C-H bond length. The Zeta 66 value is taken from reference 6. The values of L_{65}^{-1} and L_{66}^{-1} for a range of L_{64}^{-1} values obtained from the computer output are substituted in the left-hand side of (12), until left-hand side becomes equal to the right-hand side. This is how the last row of the L^{-1} matrix is fixed. The L_{4i}^{-1}'s and L_{5i}^{-1}'s are calculated using the L_{6i}^{-1} set (where $i = 4, 5, 6$).

RESULTS AND DISCUSSION

The L^{-1} matrices for the E species of CH_3Cl, CH_3Br and CH_3I are shown in tables 2–4. These

Table 2 *L^{-1} matrix of CH_3Cl (E species)*

−1.1242	−0.2833	0.0016
−0.4700	0.7831	0.2374
−0.2361	0.3211	−1.3658

Table 3 *L^{-1} matrix of CH_3Br (E species)*

−1.1337	−0.2671	0.0051
−0.4397	0.7760	0.2872
−0.2460	0.3538	−1.3709

Table 4 *L^{-1} matrix of CH_3I (E species)*

−1.2097	−0.0428	0.0987
−0.1169	0.8336	0.2154
−0.2460	0.3230	−1.3919

L^{-1} matrices are used to calculate force constants which are shown in table 5.

After the L_{6i}^{-1} row elements are fixed using Zeta equation (12), the calculation of remaining L^{-1} elements is a trivial one. In this way all the L^{-1} matrix elements are determined uniquely. This procedure actually cuts down the number of random sets for L^{-1} elements that were possible in the regular F G matrix iterative method. The force constants obtained from these L^{-1} matrices agree with those reported in literature. Specially for ν_{as}(C-H), δ(C-H_3) force constants, while the γ(C-X) mode force constant depends on the masses of the X-atoms and the nature of the C-X bond. The uncertainties reported in the intensity values were also taken into account and we have computed their effect on the force constants. It is observed that the changes that appear in the values of force constants (due to changes in intensity values) are still within the admissible range of force constants. Hence we

Table 5 *Force constants in m dynes/a.u*

Symmetric Force constant elements	Molecules		
	CH_3Cl	CH_3Br	CH_3I
F_{44}	4.83	4.50	4.90
F_{55}	0.84	0.73	0.55
F_{66}	0.78	0.65	0.60
F_{45}	0.83	0.74	0.08
F_{46}	−0.03	−0.01	−0.32
F_{56}	−0.02	0.01	−0.01

consider the intensities taken from reference 3 are reliable.

ACKNOWLEDGEMENTS

One of the authors (VD) thanks UGC, New Delhi, for a fellowship. The authors thank Dr N. Rajeswara Rao for encouragement and useful discussions.

26 October 1988; Revised 3 June 1988

1. Ravindranath, K., Dayanand, V. and Rajeswara Rao, N., *Curr. Sci.*, 1986, **55**, 562.
2. Wahegaonker, L. D. and Rajeswara Rao, N., *Pramana (J. Phys.)* 1983, **21**, 347
3. Person, W. B. and Newton, J. H., *J. Chem. Phys.*, 1976, **64**, 3036.
4. Swarna Kumari, G. and Rajeswara Rao, N., *J. Mol. Spectrosc.*, 1984, **106**, 1.
5. Meal, J. H. and Polo, S. R., *J. Chem. Phys.*, 1956, **24**, 1126.
6. Herzberg, G., *Infrared and Raman spectra of polyatomic molecules*, Van Nostrand Co., New York, 1945, p. 438.

NEWS

TRACKING A SECRET TO LOWER BLOOD PRESSURE

. . . "Strict vegetarians, who eat little if any animal products, and lactovegetarians, who regularly eat dairy products, have lower blood pressures [BPs] than the general population after adjustment for the effects of age, sex, and body weight. Controlled dietary trials were undertaken to determine the dietary basis for the differences in BP between vegetarians and non-vegetarians. Exchanging meat and eggs for vegetable products; increasing total dietary protein or replacing soy protein with dairy protein; exchanging saturated, monounsaturated, and polyunsaturated fatty acids; and changing the content of total dietary fat and carbohydrate all had no substantial effect on BP. Therefore, animal products, carbohydrate, and different types of fats do not appear to explain the low BP in vegetarians. Rather, modest intake of animal products may be a marker for a large intake of other potentially beneficial nutrients from vegetable products." Frank M. Sacks & Edward H. Kass (Harvard Univ. Brigham & Women's Hosp., Boston, MA) in *American Journal of Clinical Nutrition*, 48(3); 795–800, Sept. 88, (reproduced with permission from Press Digest, Current Contents ®, No. 50, December 12, 1988, p. 17, Published by the Institute for Scientific Information ®, Philadelphia, USA.)