Asian J Phys

CODEN

ISSN : 0971-3093

ASIAN JOURNAL OF PHYSICS

(An International Quarterly Research Journal)

Vol 5 July-September 1996 No. 3

Proceedings of the National Conference on Recent Trends in Vibrational Spectroscopy

February 26-28, 1996 — Meerut College, Meerut (INDIA)

Published by

ap

ANITA PUBLICATIONS

KC-68/1, OLD KAVI NAGAR, GHAZIABAD-201 002 (INDIA)

Phone : 011-8-40374, 011-7128751, 011-6960022

Delhi office : P.O. Box. 9280, DELHI-110092 (INDIA)

Phones : (011) 2240289, 2241051, 2423388, Fax : 011-2413388

Asian Journal of Physics

Vol 5, No 3, (1996) 225–229

Direction-cosines for barrier height determination : A general formalism

R SHANKER and R A YADAV*

Department of Physics
Banaras Hindu University, Varanasi-221005, India

In determining barrier height of a top against free rotation, one requires the direction–cosines of the top-axis relative to the principal axes. Determination of direction-cosines for a top-axis in a non-planar molecule is not straight-forward. Therefore, a general formalism to determine direction-cosines of a top-axis has been presented for the first time.

1 Introduction

Torsional oscillation of a group about a single bond relative to a comparable or larger moiety gives rise to torsional frequency usually below 350 cm^{-1}. Since thermodynamic functions of a molecule are frequency dependent and contributions for the shorter frequencies are much larger compared to those for the higher ones, the correct vibrational assignments for frequencies below 500 cm ^{1} become very important, especially if one is interested in computing the thermodynamic functions also. Once the torsional frequency of a group is assigned one can calculate classically the barrier height against free rotation for this group.

Durig *et al*[1] have presented the theory of a single top rotor i.e., for a group (like CH_3, NH_2, CHO etc.) attached to a rigid moiety by a single bond. This theory can be used for a molecule with more than one-top rotor provided the tops do not interact. However, in such a case in calculating the barrier height for one top rest of the molecule is assumed to be intact i.e., the other torsional motions are assumed to be freezed.

In computation of the barrier height one needs the torsional frequency and the reduced moment of inertia (I_r) of the corresponding top. To compute I_r one needs direction-cosines of the top-axis relative to the principal axes. Such a formalism has not been reported in the literature. The present paper deals with working out such a formalism for the first time.

Determination of direction cosines

The n-fold barrier height, V_n in cal/mol, may be computed using the Eq (1),

$$V_n = 1.02\ v^2 I_r / n^2 \qquad (1)$$

*Author for correspondence

where, ν (in cm^{-1}) is the torsional fundamental of the substituent top and I_r is the moment of inertia in unit of 10^{-39} gm-cm^2. The reduced moment of inertia (I_r) is defined by,

$$I_r = I_\alpha[1 - I_\alpha(\lambda_A^2 / I_A + \lambda_B^2 / I_B + \lambda_C^2 / I_C) \quad (2)$$

where, I_α is the moment of inertia of the top about its own axis and can be determined easily; I_A, I_B and I_C are the principal moments of inertia and λ_A, λ_B, and λ_C are the direction-cosines of the top-axis with respect to the principal axes.

The principal moments of inertia (I_A, I_B and I_C) are determined by using the relation due to Hirschfelder[2],

$$\begin{vmatrix} a-I & -d & -e \\ -d & b-I & -f \\ -e & -f & c-I \end{vmatrix} \quad (3)$$

The definitions of the quantities *a, b, c, d, e* and *f* can be found in standard texts of Colthup *et al*[3]. In the above equation the quantities *a, b* and *c* are always non-zero whereas each of the quantities *d, e* and *f* may have positive/zero/ negative values depending upon the structure of the molecule and the chosen molecule-fixed cartesian coordinate system. These quantities (*a, b, c, d, e* and *f*) are determined in terms of cartesian coordinate with respect to the molecule fixed cartesian coordinate system and masses of all atoms. The roots of the cubic equation (3) are the three principal moments of inertia.

For a molecule having C_s symmetry atleast two of the three quantities *d, e* and *f* are zero and hence the roots of the Eq. (3) and the values of λ_A, λ_B and λ_C are easily determined. However, for the non-zero values of *d, e* and *f* analytical factorization of Eq. (3) is not possible and therefore, one has to use the numerical method of factorization. Bairstows method[4] of numerical factorization has been used to evaluate I_A, I_B and I_C. In such a case the determination of λ_A, λ_B and λ_C is not straight forward. The method to evaluate λ_A, λ_B and λ_C for a general case (non-zero *d, e* and *f*) is not available in literature. Therefore, a general formalism of the problem to evaluate λ_A, λ_B and λ_C has been worked out in the present case for the first time and is given below:

The matrix equation,

$$\begin{vmatrix} a-I & -d & -e \\ -d & b-I & -f \\ -e & -f & c-I \end{vmatrix} \begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} 0 \\ 0 \\ 0 \end{vmatrix} \quad (4)$$

can be used to find the directions of the three principal axes from the following three equations,

$$(a\text{–I})x - dy - ez = 0 \tag{4a}$$
$$-dx + (b\text{–I})y - fz = 0 \tag{4b}$$
$$-ex - fy + (c\text{–I})z = 0 \tag{4c}$$

Eqs. (4a) and (4b) lead to the following relation,

$$x{:}y{:}z = [(b\text{–I})e+fd] : [(a\text{–I})f+ed] : [(a\text{–I})(b\text{–I})-d^2] \tag{5}$$

Assuming, $l_0 = (b\text{–I})\,e+fd$; $m_0 = (a\text{–I})f+ed$ and $n_0 = (a\text{–I})(b\text{–I})-d^2$, one may get the direction-cosines l, m and n of I_A, I_B and I_C axes with respect to the molecule fixed cartesian coordinate system as,

$$l = l_0 (l_0^2 + m_0^2 + n_0^2)^{-1/2} \tag{6a}$$
$$m = m_0 (l_0^2 + m_0^2 + n_0)^{-1/2} \tag{6b}$$
$$n = n_0 (l_0^2 + m_0^2 + n_0^2)^{-1/2} \tag{6c}$$

Therefore, the unit vector along a principal axis with the principal moment as I may be written as,

$$\hat{U} = l\hat{i} + m\hat{j} + n\hat{k} \tag{7}$$

where, $\hat{i}$, $\hat{i}$ and $\hat{k}$ are the unit vectors along the molecule fixed x, y and z axes, respectively. For $I = I_A$, I_B and I_C one has three sets of l, m and n corresponding to the three principal axes (I_A, I_B and I_C) and therefrom, one has the three unit vectors along the three principal axes, namely, $\hat{U}_A$, $\hat{U}_B$ and $\hat{U}_C$.

The unit vector along a top axis is given by,

$$\hat{U}' = l'\hat{i} + m'\hat{j} + n'\hat{k} \tag{8}$$

where, l', m' and n' are the direction-cosines of the unit vector along the top-axis with respect to the molecule-fixed cartesian coordinate axes. The values of l', m' and n' are easily determined with the help of the top axis and the molecule-fixed cartesian coordinate system and thus, one can determine the unit vector $\hat{U}'$ along a given top-axis. The cosine of the angle θ between this unit vector (Eq. 8) and the unit vector along a principal axis given by Eq. (7) may be determined by the dot product of Eqs. (7) and (8) and is given by,

$$\cos\theta = \lambda = ll' + mm' + nn' \tag{9}$$

Using Eq. (9), for the three principal moments of inertia I_A, I_B and I_C, one gets three values of λ, namely λ_A, λ_B and λ_C, respectively, i.e., if one substitutes in Eq. (9) the values of l, m and n for the principal axis corresponding to I_A one gets λ_A and so on.

Example

Though the present formalism is a general one and can be used for any (planar or non-planar) molecule its applicability is illustrated here for the case

Table 1. Barrier height and related quantities for the isomeric-TFM anilines

#	*o*-TFM aniline	*m*-TFM aniline	*p*-TFM aniline
I_α (CF_3)	15.3177	15.3177	15.3177
I_α (NH_2)	0.2528	0.2528	0.2538
a	116.9120	136.9280	146.9280
b	87.6603	107.6760	131.8380
c	44.6444	44.6444	30.4833
d	0.2967	0.2967	0.000001
e	0.0120	− 0.3305	− 0.5015
f	− 0.4912	− 16.8437	− 0.0007
I_A	44.6388 (44.7030)	40.4242 (40.4505)	30.4811 (30.4534)
I_B	87.6629 (87.6462)	111.8932 (111.9740)	131.8376 (132.0100)
I_C	116.9148 (117.0378)	136.9311 (137.1133)	146.9311 (147.1524)
$\hat{U}_A$	$0.0000\hat{i}$ −0.011389 $\hat{j}$ +0.999935 $\hat{k}$	− 0.004047 $\hat{i}$ − 0.242889 $\hat{j}$ +0.970046 $\hat{k}$	− 0.004294 $\hat{i}$ −0.000007 $\hat{j}$ +0.999991 $\hat{k}$
$\hat{U}_B$	− 0.009916 $\hat{i}$ −0.999934 $\hat{j}$ − 0.005869 $\hat{k}$	− 0.008037 $\hat{i}$ − 0.970079 $\hat{j}$ − 0.242658 $\hat{k}$	*0.01 $\hat{i}$ −*1.0 $\hat{j}$ + *0.0 $\hat{k}$
$\hat{U}_C$	− 0.981766 $\hat{i}$ +0.006551 $\hat{j}$ − 0.189983 $\hat{k}$	0.999643 $\hat{i}$ − 0.020060 $\hat{j}$ − 0.017629 $\hat{k}$	*1.0 $\hat{i}$ +*0.0 $\hat{j}$ +*0.0 $\hat{k}$
$\hat{U}'(CF_3)$	$0.0\hat{i}$ +0.0 $\hat{j}$ +1.0 $\hat{k}$	$0.0\hat{i}$ +0.0 $\hat{j}$ +1.0 $\hat{k}$	$0.0\hat{i}$ +0.0 $\hat{j}$ +1.0 $\hat{k}$
$\hat{U}'(NH_2)$	$0.0\hat{i}$ + √3/2 $\hat{j}$ +1/2 $\hat{k}$	$0.0\hat{i}$ + √3/2 $\hat{j}$ −1/2 $\hat{k}$	$0.01\hat{i}$ +0.0 $\hat{j}$ −1.0 $\hat{k}$
$\lambda_A(CF_3)$	− 0.999993	0.970046	0.999991
λ_B (CF_3)	− 0.005869	− 0.242658	0.0
λ_C (CF_3)	− 0.189983	− 0.017629	0.0
$\lambda_A(NH_2)$	0.490104	− 0.695371	− 0.999991
$\lambda_B(NH_2)$	− 0.868903	− 0.961442	0.0
λ_C (NH_2)	− 0.089318	− 0.026119	0.0
$I_\gamma(CF_3)$	9.9812 (10.0700)	9.7321 (9.9320)	7.6202 (7.6130)
I_γ (NH_2)	0.2519 (0.2521)	0.2515 (0.2519)	0.2507 (0.2509)
V_3 (CF_3)	6.3656 (6.4222)	5.4067 (5.4067)	4.2334 (4.2294)
V_2 (NH_2)	2.9143 (2.9166)	3.3337 (3.3392)	3.3233 (3.3259)

The units of *a*, *b*, *c*, *d*, *e*, *f*, I_A, I_B, I_C, I_α and I_γ are 10^{-39} gm cm^2; unit of V_n kcal/mole.

of three isomeric-trifluoromethyl anilines (*o*–, *m*– and *p*– $CF_3.C_6H_4.NH_2$), as these molecules are non-planar and have no symmetry. Hence, the quantities *d*,

e and *f* have non-zero values and thus, these molecules form a general case of example.

The torsional frequency of the CF_3 group has a magnitude around 65 cm^{-1} whereas that of NH_2 group has varying magnitude in the region 200–500 cm^{-1} Moreover, the CF_3 group is a very intact moeity on account of the most electronegative nature of the fluorine atoms. Therefore, to a first approximation the two tops may be taken to be non-interacting and the single-top theory of Durig *et al*[1] may be used to compute the barrier heights for the CF_3 and NH_2 groups.

To compute the barrier heights for the three isomerictrifluoromethyl anilines structural parameters have been taken from the work of Shanker[5]. Bond lengths (r) and bond angles ($\angle$) are; r(C–F) = 1.344 Å, r(C–CF_3) = 1.481 Å, r(N–H) = 1.0 Å, r(C–N) = 1.42 Å, r(C–C) = 1.397 Å, r(C–H) = 1.084 Å, $\angle$FCF = $\angle$FCC = 109° 28′, $\angle$C–C–CF_3 = 120°, $\angle$C–C–N = 120°, $\angle$C–C–C = $\angle$C–C–H = 120°, $\angle$HNH = 115° and the angle between the phenyl-ring plane and the NH_2 group, ϕ = 40°.

For computing barrier heights the torsional frequencies for the CF_3 top are 75, 70 and 70 cm^{-1} and for the NH_2 top 213, 228 and 228 cm^{-1}, respectively for the *o*–, *m*– and *p*– isomers[5]. The other quantities have been calculated for the three-isomeric-trifluoromethyl anilines and collected in Table 1. The reduced moments of inertia (I_r) and the barrier heights (V_n) for the CF_3 (n = 3) and NH_2 (n=2) tops have also been determined with the structure given above and with ϕ = 0° i.e., the NH_2 group co-planar with the phenyl-ring, keeping other things identical. The quantities for the latter structure are given in parentheses in Table 1.

From Table 1 one can see that the quantities I_r and V differ by ~ 0.5% for the two structures (one in which NH_2 group plane makes 40° with the phenyl-ring and the other in which NH_2 group is co-planar with the phenyl-ring). Thus, one can assume the NH_2 group co-planar with the phenyl-ring for the purpose of barrier height determination.

References

1 Durig R, Craven S M & Harris W C, *Vibrational Spectra and Structure*, Vol 1, Edited by J R Durig, (Marcel Dekker Inc, N Y), 1972 p 73.

2 Hirschfelder J O, *J Chem Phys*, 8, (1940) 431.

3 Colthup N B, Daly L H & Wiberley S E, *Introduction to Infrared and Raman spectroscopy*, (Academic press, N Y and London) 1964.

4 Gerald C F, *Applied Numerical Analysis*, 2nd Edn. (Addison-Wesley Publishing Co, Inc Cambridge, Mass (USA), page 50, (1978).

5 Shanker R, Ph D Thesis, Banaras Hindu University, India (1991).

[*Received* 12.2.1996; *accepted* 16.2.1996]