MEAN AMPLITUDES OF VIBRATION: BENT XYZ MOLECULES

BY DR. K. VENKATESWARLU, F.A.Sc.
AND
DR. S. MARIAM

(Department of Physics, Kerala University, C/o U.C. College, Alwaye, S. India)

Received August 22, 1964

ABSTRACT

The theory of mean-square amplitude matrices is applied to the bent XYZ molecules. The principal mean amplitudes of vibration for the molecules investigated here are reported for 300° K.

INTRODUCTION

The study of mean amplitudes of vibration is of great interest for electron diffraction investigations. It provides an additional set of parameters required in defining the nonrigid model of the molecules. It serves as an additional information to normal frequencies in the determination of a complete harmonic force field. The theory of computing the mean amplitudes of vibration from spectroscopic data is developed by Morino and Hirota.¹ A slightly modified method is suggested by Cyvin,² who gave a new secular equation, relating the mean-square amplitudes of vibration to the normal frequencies. In this investigation, Cyvin's method has been applied to the evaluation of mean amplitudes of ten bent XYZ molecules at 300° K. using their vibrational frequencies. All the bonded and nonbonded mean square amplitude quantities and the corresponding mean amplitude quantities of these molecules are reported here for the first time.

2. SYMMETRY CO-ORDINATES

The bent XYZ molecules (Fig. 1) belong to the point group C₈ and possess three A' normal modes of vibration.

The following are the symmetry co-ordinates formed out of the valence force co-ordinates ΔD, ΔR and Δα, where D, R and α denote the equilibrium values.

260
Mean Amplitudes of Vibration: Bent $XYZ_2$ Molecules

$S_1 = \Delta D$

$S_2 = \Delta R$

$S_3 = (DR)^\delta \triangle \alpha$.

The angle displacement co-ordinate has been multiplied by $(DR)^\delta$ in order to have the same dimension to all the symmetry co-ordinates.

![Configuration of bent $XYZ$ molecules.](image)

**Fig. 1.** Configuration of bent $XYZ$ molecules.

3. **Symmetrized Mean-Square Amplitude Matrix**

The harmonic potential energy function for $XYZ$ molecules is given below in terms of the valence force co-ordinates.

$$2V = f_D (\Delta D)^2 + f_R (\Delta R)^2 + f_\alpha (\Delta \alpha)^2 + 2f_{DR} (\Delta D) (\Delta R)$$

$$+ 2f_{Da} (\Delta D) (\Delta a) + 2f_{Ra} (\Delta R) (\Delta a).$$

Where $f_D$ and $f_R$ are the XY and YZ stretching constants respectively, $f_\alpha$ the bending constant and $f_{DR}, f_{Da}, f_{Ra}$ are the interaction constants concerning the respective parameters.

Using the above potential function, the symmetrized mean-square amplitude matrix $\Sigma$ is formed and the elements of $\Sigma$ matrix are given below in terms of the symmetry co-ordinates.

$$\Sigma_{11} = \langle S_1^2 \rangle = \sigma_D$$

$$\Sigma_{22} = \langle S_2^2 \rangle = \sigma_R$$

$$\Sigma_{33} = \langle S_3^2 \rangle = \sigma_\alpha$$

$$\Sigma_{12} = \langle S_1 S_2 \rangle = \sigma_{DR}$$

$$\Sigma_{13} = \langle S_1 S_3 \rangle = \sigma_{Da}$$

$$\Sigma_{23} = \langle S_2 S_3 \rangle = \sigma_{Ra}$$
4. **ADDITIONAL MEAN-SQUARE AMPLITUDE**

Considering the nonbonded distance deviation $\Delta r^*$, the following additional mean-square amplitude quantity is obtained in terms of the symmetrized mean-square amplitude matrix elements.

$$
\sigma_{r^*} = \langle (\Delta r^*)^2 \rangle
$$

$$
= \frac{1}{r^{\#2}} \left[ A^2 \sigma_D + B^2 \sigma_R + C^2 \sigma_a + 2AB \sigma_{DR} + 2BC \sigma_{Ra} + 2AC \sigma_{Da} \right].
$$

Where $r^*$ is the interatomic displacement between nonbonded atoms, $A = (D - R \cos \alpha)$, $B = (R - D \cos \alpha)$, $C = (DR)^{1/2} \sin \alpha$ and $r^* = (D^2 + R^2 - 2DR \cos \alpha)^{1/2}$.

5. **G MATRIX**

Using Wilson’s method the following $G$ matrix elements are obtained:

$$
G_{11} = \mu_x + \mu_y
$$

$$
G_{22} = \mu_z + \mu_y
$$

$$
G_{33} = DR \left[ \frac{\mu_x}{D^2} + \frac{\mu_z}{R^2} \right] + (DR) \frac{\mu_y}{\sin^2 \alpha} \left[ \left( \frac{1}{R} - \frac{\cos \alpha}{D} \right)^2 + \left( \frac{1}{D} - \frac{\cos \alpha}{R} \right)^2 + 2 \left( \frac{1}{R} - \frac{\cos \alpha}{D} \right) \left( \frac{1}{D} - \frac{\cos \alpha}{R} \right) \cos \alpha \right]
$$

$$
G_{12} = \mu_y \cos \alpha
$$

$$
G_{13} = - (DR)^{1/2} \frac{\mu_y}{\sin \alpha} \left[ \left( \frac{1}{R} - \frac{\cos \alpha}{D} \right)^2 + \left( \frac{1}{D} - \frac{\cos \alpha}{R} \right)^2 \cos \alpha \right]
$$

$$
G_{23} = - (DR)^{1/2} \frac{\mu_y}{\sin \alpha} \left[ \left( \frac{1}{D} - \frac{\cos \alpha}{R} \right)^2 + \left( \frac{1}{R} - \frac{\cos \alpha}{D} \right) \cos \alpha \right].
$$

6. **RESULTS AND DISCUSSION**

The elements of the mean-square amplitude matrix $\Sigma$ were obtained by solving the secular equation

$$
| \Sigma G^{-1} - E \Delta | = 0
$$

where $G^{-1}$ is the inverse of the kinetic energy matrix and $E$ is the unit Matrix. The values of $\Delta$ are connected with the normal frequencies $\nu_k$ by the relation
Mean Amplitudes of Vibration: Bent XYZ₂ Molecules

\[ \Delta k = \frac{h}{8\pi^2 v_k} \coth \left( \frac{h v_k}{2k T} \right) \]

where \( h \) is the Planck's constant, \( k \) is the Boltzmann's constant and \( T \) absolute temperature.

The molecular parameters and the observed fundamental frequencies of the molecules studied in this investigation are given in Table I.

The mean-square amplitudes of vibration evaluated for the bonded and nonbonded distances respectively are listed in Table II.

The mean amplitude quantities, \( \sigma_D \), \( \sigma_R \) and \( \sigma_T \), are given in Table III.

It can be seen from the results presented in Table III that the mean amplitudes of vibration for some bonded interatomic distances are found to possess characteristic values, namely, nearly 0.0695 for OH bond in HDO and HOCI molecules and 0.04226 for N = O bond in the nitrosyl compounds. The mean amplitude values for nitrogen halogen bond in nitrosyl compounds increase from lower to higher members of the series and the same trend is noted for the oxygen-halogen nonbonded distances also but the increase is more rapid in the case of nonbonded mean amplitudes.

**Table I**

Molecular parameters and observed frequencies (cm⁻¹) of bent XYZ molecules

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Bond angle</th>
<th>Bond length (Å)</th>
<th>Observed frequencies (cm⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>R</td>
<td>( v_1 )</td>
</tr>
<tr>
<td>DOH</td>
<td>104° 31'</td>
<td>0.958</td>
<td>0.958</td>
<td>2727</td>
</tr>
<tr>
<td>DSH</td>
<td>92°</td>
<td>1.345</td>
<td>1.345</td>
<td>1078</td>
</tr>
<tr>
<td>DSeH</td>
<td>91°</td>
<td>1.47</td>
<td>1.47</td>
<td>1691</td>
</tr>
<tr>
<td>O¹⁶SO¹⁸</td>
<td>120°</td>
<td>1.46</td>
<td>1.46</td>
<td>1122</td>
</tr>
<tr>
<td>HOCI</td>
<td>113°</td>
<td>0.957</td>
<td>1.7</td>
<td>3626</td>
</tr>
<tr>
<td>DOCI</td>
<td>113°</td>
<td>0.957</td>
<td>1.7</td>
<td>2674</td>
</tr>
<tr>
<td>ONF</td>
<td>110°</td>
<td>1.13</td>
<td>1.52</td>
<td>1844</td>
</tr>
<tr>
<td>ON¹³Cl</td>
<td>116°</td>
<td>1.14</td>
<td>1.95</td>
<td>1760</td>
</tr>
<tr>
<td>ON¹⁴Cl</td>
<td>116°</td>
<td>1.14</td>
<td>1.95</td>
<td>1800</td>
</tr>
<tr>
<td>ONBr</td>
<td>117°</td>
<td>1.15</td>
<td>2.14</td>
<td>1801</td>
</tr>
</tbody>
</table>
### Table II

*Mean-square amplitudes ($\text{Å}^2$) of bent XYZ molecules at 300°C K.*

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$\sigma_D$</th>
<th>$\sigma_R$</th>
<th>$\sigma_a$</th>
<th>$\sigma_r^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOH</td>
<td>0.003373</td>
<td>0.004884</td>
<td>0.019351</td>
<td>0.013321</td>
</tr>
<tr>
<td>DSH</td>
<td>0.004145</td>
<td>0.005663</td>
<td>0.031172</td>
<td>0.014034</td>
</tr>
<tr>
<td>DSeH</td>
<td>0.005188</td>
<td>0.007268</td>
<td>0.027283</td>
<td>0.020198</td>
</tr>
<tr>
<td>O\textsuperscript{18}SO\textsuperscript{18}</td>
<td>0.001561</td>
<td>0.001432</td>
<td>0.006419</td>
<td>0.009091</td>
</tr>
<tr>
<td>HOCl</td>
<td>0.004801</td>
<td>0.001748</td>
<td>0.038193</td>
<td>0.010543</td>
</tr>
<tr>
<td>DOCl</td>
<td>0.004661</td>
<td>0.001748</td>
<td>0.020324</td>
<td>0.007285</td>
</tr>
<tr>
<td>ONF</td>
<td>0.001786</td>
<td>0.003249</td>
<td>0.010122</td>
<td>0.003345</td>
</tr>
<tr>
<td>ON\textsuperscript{18}Cl</td>
<td>0.001579</td>
<td>0.003215</td>
<td>0.013491</td>
<td>0.004272</td>
</tr>
<tr>
<td>ON\textsuperscript{14}Cl</td>
<td>0.001786</td>
<td>0.003311</td>
<td>0.013934</td>
<td>0.005148</td>
</tr>
<tr>
<td>ONBr</td>
<td>0.001788</td>
<td>0.003481</td>
<td>0.014582</td>
<td>0.006061</td>
</tr>
</tbody>
</table>

### Table III

*Mean amplitudes (Å) of bent XYZ molecules at 300°C K.*

<table>
<thead>
<tr>
<th>Distance</th>
<th>(X – Y)</th>
<th>(Y – Z)</th>
<th>(X...Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOH</td>
<td>0.05808</td>
<td>0.06988</td>
<td>0.11661</td>
</tr>
<tr>
<td>DSH</td>
<td>0.06512</td>
<td>0.07518</td>
<td>0.11842</td>
</tr>
<tr>
<td>DSeH</td>
<td>0.07202</td>
<td>0.08526</td>
<td>0.14211</td>
</tr>
<tr>
<td>O\textsuperscript{18}SO\textsuperscript{18}</td>
<td>0.03951</td>
<td>0.03785</td>
<td>0.09535</td>
</tr>
<tr>
<td>HOCl</td>
<td>0.06929</td>
<td>0.04184</td>
<td>0.10269</td>
</tr>
<tr>
<td>DOCl</td>
<td>0.06828</td>
<td>0.04184</td>
<td>0.08525</td>
</tr>
<tr>
<td>ONF</td>
<td>0.04226</td>
<td>0.05701</td>
<td>0.05784</td>
</tr>
<tr>
<td>ON\textsuperscript{18}Cl</td>
<td>0.03973</td>
<td>0.05671</td>
<td>0.06536</td>
</tr>
<tr>
<td>ON\textsuperscript{14}Cl</td>
<td>0.04226</td>
<td>0.05754</td>
<td>0.07176</td>
</tr>
<tr>
<td>ONBr</td>
<td>0.04229</td>
<td>0.05899</td>
<td>0.07785</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENT

One of the authors (S.M.) is thankful to the Council of Scientific and Industrial Research, Government of India, New Delhi, for the award of a Senior Research Fellowship.

REFERENCES