THEORETICAL DESCRIPTION OF INFRARED AND RAMAN SPECTRA OF XY₃ZWAB TYPE MOLECULES

S MOHAN* AND FERIDOUN PAYAMI

Division of Applied Sciences, Madras Institute of Technology, Anna University,
Chromepet, Madras 600 044, India

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A complete vibrational analysis has been carried out using kinetic constants for methylthynylmercury (II) and its isotopes and a set of molecular constants viz., potential constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants is reported for the first time. The values of these molecular constants fall in the expected range and they are reasonable. Further, it is shown that kinetic constant method leads to acceptable sets of characteristic constants for CH₃HgCCH, CH₃HgCCD, CD₃HgCCH and CD₃HgCCD molecules. The molecular character of the bonds is briefly discussed.

Key Words: Infrared and Raman Spectra; XY₃ZWAB Type Molecules; Kinetic Constants; Methylthynylmercury (II); Molecular Constants

INTRODUCTION

It has been noted that the kinetic constants of molecules appear to be of fundamental significance and of some use in evaluating reasonable sets of potential constants. The procedure of kinetic constants has been applied by Mohan et al.¹−⁵ to obtain acceptable sets of potential constants in different types of polyatomic molecules. These potential constants have also led to significant results of molecular constants such as mean amplitudes of vibration, Coriolis coupling constants, centrifugal distortion constants, shrinkage constants, dipole moments and inertia defects. The calculated values of these molecular constants are further found to be in good agreement with the corresponding observed values, wherever available, thus establishing the merits of the new procedure involving kinetic constants. Such initial studies were confined to 2 × 2, 3 × 3, 4 × 4 and 5 × 5 vibrational problems whereas an example of the 6 × 6 vibrational problem has been examined in this paper with success for the first time.

The purpose of the present investigation is to adopt the procedure of kinetic constants in the evaluation of the potential constants and other molecular constants of methylthynylmercury molecule and its isotopes which involve 6 × 6 vibrational problems. For the molecular type under study the kinetic constants have been worked out and they have been utilised to solve the secular equation in an elegant manner and thereby study the different molecular constants.

*Present Address: Department of Physics, Pondicherry University, Pondicherry 605 006.
THEORETICAL CONSIDERATIONS

Methylethynylmercury molecule assumes C\textsubscript{3v} molecular symmetry from group theoretical considerations. Since it is well known that the C-Hg-C skeleton in many organomercurials (II) is linear\textsuperscript{6}, it is reasonable to assume the same skeleton for the present compound. Accordingly there are twelve fundamental vibrations distributed as 6\textit{A}\textsubscript{1} + 6\textit{E}. All of them are active both in Raman and infrared spectra. The symmetry coordinates used in the present work are given below:

\textit{A}\textsubscript{1} Species

\begin{align*}
S_1 &= \Delta t \\
S_2 &= \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3) \\
S_3 &= \Delta D \\
S_4 &= \frac{1}{\sqrt{6}} \left[ r(\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3) - \sqrt{rR} (\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3) \right] \\
S_5 &= \Delta R \\
S_6 &= \Delta d
\end{align*}

\textit{E} Species

\begin{align*}
S_{7a} &= \frac{1}{\sqrt{6}} (2\Delta r_1 - \Delta r_2 - \Delta r_3) \\
S_{7b} &= \frac{1}{\sqrt{2}} (\Delta r_2 - \Delta r_3) \\
S_{8a} &= \frac{r}{\sqrt{6}} (2\Delta \alpha_1 - \Delta \alpha_2 - \Delta \alpha_3) \\
S_{8b} &= \frac{r}{\sqrt{2}} (\Delta \alpha_2 - \Delta \alpha_3) \\
S_{9a} &= \sqrt{\frac{rR}{6}} (2\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3) \\
S_{9b} &= \sqrt{\frac{rR}{2}} (\Delta \beta_2 - \Delta \beta_3) \\
S_{10a} &= \sqrt{Dt} \Delta \phi_a \\
S_{10b} &= \sqrt{Dt} \Delta \phi_b \\
S_{11a} &= \sqrt{Dd} \Delta \theta_a \\
S_{11b} &= \sqrt{Dd} \Delta \theta_b \\
S_{12a} &= \sqrt{Rd} \Delta \gamma_a \\
S_{12b} &= \sqrt{Rd} \Delta \gamma_b
\end{align*}

where \( \Delta t, \Delta r, \Delta D, \Delta R \) and \( \Delta d \) are the changes in bond distances and \( \Delta \alpha, \Delta \beta, \) etc., denote the changes in bond angles.

The most general quadratic potential energy function in terms of internal coordinates has been considered and hence \textit{G}-matrix elements have been obtained. They are...
$A_1$ Species

\[
\begin{bmatrix}
f_t & 3f_{rt} & f_{Dt} & \sqrt{\frac{3}{2}} \left(f_{ta} - f_{t\beta}\right) & f_{Rt} & f_{dt} \\
f_r + 2f_{rr} & 3f_{rd} & \sqrt{\frac{1}{\sqrt{2}}} \left(f'_{ra} + 2f_{ra} - f_{r\beta} - 2f'_{r\beta}\right) & \sqrt{3}f_{rR} & \sqrt{3}f_{rd} \\
f_D & \sqrt{\frac{3}{2}} \left(f_{Da} - f_{DB}\right) & f_{RD} & f_{aD} \\
\frac{1}{2} \left(f_a + 2f_{a\alpha}\right) - \left(f_a + 2f'_{a\alpha}\right) \sqrt{\frac{3}{2}} \left(f_{Ra} - f_{R\beta}\right) & \sqrt{3} \left(f_{da} - f_{d\beta}\right) & \sqrt{3} \left(f_{da} - f_{d\beta}\right) \\
+ \frac{1}{6} \left(f_{\beta} + 2f_{\beta\beta}\right) & & & \\
\text{SYMMETRIC} & f_R & f_{Rd} & f_d
\end{bmatrix}
\]

$E$ Species

\[
\begin{bmatrix}
f_{rr} & \frac{1}{6} \left(f'_{ra} - 3f'_{ra}\right) & \left(f_{r\beta} - f_{r\beta} / 3\right) & \frac{1}{\sqrt{6}} f_{r\phi} & \frac{1}{\sqrt{6}} f_{r\phi} & \frac{1}{\sqrt{6}} f_{r\gamma} \\
\left(f_a - f_{a\alpha}\right) & \left(f_{a\beta} - f_{a\beta}\right) & \frac{1}{\sqrt{6}} f_{a\phi} & \frac{1}{\sqrt{6}} f_{a\phi} & \frac{1}{\sqrt{6}} f_{a\gamma} \\
\left(f_{\beta} - f_{\beta\beta}\right) & \frac{2}{\sqrt{6}} f_{\beta\phi} & \frac{2}{\sqrt{6}} f_{\beta\phi} & \frac{2}{\sqrt{6}} f_{\beta\gamma} \\
\text{SYMMETRIC} & f_{\phi} & f_{\phi} & f_{\gamma} & f_{\gamma}
\end{bmatrix}
\]

On the basis of Wilson's formula, $G$ matrix elements have been evaluated. The kinetic constants derived from a knowledge of $G$-matrix elements using Wilson's expression $2T = \tilde{S} G^{-1} \tilde{S}$.

The method of kinetic constants for evaluating the force constants has been found to give quite similar results in different molecular types as mentioned earlier.$^{1-5}$ The determination of symmetry force constants involved in the secular equation from the $n_1$ vibrational frequencies alone has been a mathematically underdetermined problem so far. Therefore any genuine attempt to evaluate all the symmetry force constants associated with a problem in the order of $n > 1$ should involve the incorporation of at least $n_1(n_1 - 1)/2$ additional data other than the $n_1$ frequencies. The procedure of kinetic constants seem to relate the off-diagonal elements to the diagonal elements of the $F$-matrix through the relation

$$
\frac{F_{ij}}{F_{ii}} = \frac{K_{ij}}{K_{ii}} \quad (i < j; i, j = 1, 2, 3, 4, 5, 6)
$$
Thus the equations involving \( A_1 \) species and \( E \) species are solved easily.

**Vibrational Mean Amplitudes**

Utilising Cyvin's equation (8) \( \Sigma = L \Delta L' \), the symmetrized mean square amplitudes and hence the valence mean square amplitude-quantities for both the bonded and non-bonded distances are evaluated at 298.16 \( K \) using the present set of force constants. On the basis of these values the mean amplitudes of vibration for these molecules are evaluated. The shortening or shrinkage of bond distances are also calculated using perpendicular mean square amplitudes.

**Coriolis Coupling Constants**

Coriolis vibration-rotation constants \( \zeta^\alpha (\alpha = X, Y, Z) \) in this type of molecules arise from the couplings \( E \times E (Z-\text{axis}) \) and \( A_1 \times E (X, Y \text{ axis}) \). The Coriolis matrix elements \( C^\alpha_{ij} (\alpha = X, Y, Z) \) are obtained according to the vector method of Meal and Polo. The \( \zeta \) — matrices related to the \( C^\alpha \) matrices by relation having the form

\[
\zeta^\alpha = L^{-1} C^\alpha (L^{-1})'
\]

where \( L \) is the normal coordinate transformation matrix.

**Centrifugal Distortion Constants**

The centrifugal distortion constants are evaluated using Cyvin's reformulated theory.\(^{10}\)

**Results and Discussion**

The structural parameters and the vibrational frequencies of the molecules under study are given in Table 1. Due to lack of the structural data of \( \text{CH}_3\text{HgCCH} \) molecule, the structural parameters have been transferred from allied molecules.

<table>
<thead>
<tr>
<th>( A_1 ) species</th>
<th>( \text{CH}_3\text{HgCCH} )</th>
<th>( \text{CH}_3\text{HgCCD} )</th>
<th>( \text{CD}_2\text{HgCCH} )</th>
<th>( \text{CD}_2\text{HgCCD} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3288</td>
<td>2567</td>
<td>3292</td>
<td>2572</td>
<td></td>
</tr>
<tr>
<td>2908</td>
<td>2903</td>
<td>2126</td>
<td>2126</td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>1885</td>
<td>2013</td>
<td>1891</td>
<td></td>
</tr>
<tr>
<td>1201</td>
<td>1204</td>
<td>935</td>
<td>934</td>
<td></td>
</tr>
<tr>
<td>559</td>
<td>557</td>
<td>507</td>
<td>506</td>
<td></td>
</tr>
<tr>
<td>( E ) species</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>440</td>
<td>431</td>
<td>435</td>
<td>426</td>
<td></td>
</tr>
<tr>
<td>2980</td>
<td>2977</td>
<td>2236</td>
<td>2239</td>
<td></td>
</tr>
<tr>
<td>1410</td>
<td>1412</td>
<td>1031</td>
<td>1030</td>
<td></td>
</tr>
<tr>
<td>779</td>
<td>780</td>
<td>591</td>
<td>591</td>
<td></td>
</tr>
<tr>
<td>655</td>
<td>514</td>
<td>656</td>
<td>514</td>
<td></td>
</tr>
<tr>
<td>272</td>
<td>262</td>
<td>276</td>
<td>257</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>95</td>
<td>93</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

\[ r = 1.1; R = 2.08; d = 2.05; D = 1.21; t = 1.06 \]
\[ \alpha = \beta = 109.28^\circ; \gamma = \theta = \phi = 180^\circ \]
viz., CH$_3$HgCl, CH$_3$HgCN and CH$_3$CCH. The valence force constants for all the four molecules are listed in Table II.

<table>
<thead>
<tr>
<th>Table II</th>
<th>Valence force constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_3$HgCCH</td>
</tr>
<tr>
<td>$f_{s}(X-Y)$</td>
<td>4.5026</td>
</tr>
<tr>
<td></td>
<td>(4.676)</td>
</tr>
<tr>
<td>$f_{R}(X-Z)$</td>
<td>2.6254</td>
</tr>
<tr>
<td></td>
<td>(2.538)</td>
</tr>
<tr>
<td>$f_{d}(Z-W)$</td>
<td>2.7006</td>
</tr>
<tr>
<td></td>
<td>(2.832)</td>
</tr>
<tr>
<td>$f_{D}(W≡A)$</td>
<td>14.6851</td>
</tr>
<tr>
<td>$f_{s}(A-B)$</td>
<td>5.5861</td>
</tr>
<tr>
<td></td>
<td>(5.752)</td>
</tr>
<tr>
<td>$f_{rr}$</td>
<td>-0.0867</td>
</tr>
<tr>
<td></td>
<td>(-0.063)</td>
</tr>
<tr>
<td>$f_{RR}$</td>
<td>-0.1986</td>
</tr>
<tr>
<td></td>
<td>(-0.1856)</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>0.1125</td>
</tr>
<tr>
<td>$f_{D}$</td>
<td>-0.2894</td>
</tr>
<tr>
<td></td>
<td>(-0.2368)</td>
</tr>
<tr>
<td>$f_{t}$</td>
<td>0.5127</td>
</tr>
<tr>
<td>$f_{Rd}$</td>
<td>-0.1367</td>
</tr>
<tr>
<td></td>
<td>(-0.134)</td>
</tr>
<tr>
<td>$f_{RD}$</td>
<td>0.2651</td>
</tr>
<tr>
<td></td>
<td>(0.2421)</td>
</tr>
<tr>
<td>$f_{RI}$</td>
<td>-0.1765</td>
</tr>
<tr>
<td></td>
<td>(-0.0981)</td>
</tr>
<tr>
<td>$f_{DD}$</td>
<td>-0.2715</td>
</tr>
<tr>
<td></td>
<td>(-0.1986)</td>
</tr>
<tr>
<td>$f_{Dd}$</td>
<td>-0.2622</td>
</tr>
<tr>
<td></td>
<td>(-0.2086)</td>
</tr>
<tr>
<td>$f_{DD}$</td>
<td>-0.1826</td>
</tr>
<tr>
<td></td>
<td>(-0.0825)</td>
</tr>
<tr>
<td>$f_{a}$</td>
<td>0.2678</td>
</tr>
<tr>
<td>$f_{B}$</td>
<td>0.1421</td>
</tr>
<tr>
<td></td>
<td>(0.1421)</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>0.0702</td>
</tr>
<tr>
<td></td>
<td>(0.0714)</td>
</tr>
<tr>
<td>$f_{a}$</td>
<td>0.1681</td>
</tr>
<tr>
<td></td>
<td>(0.1986)</td>
</tr>
<tr>
<td>$f_{B}$</td>
<td>0.2222</td>
</tr>
<tr>
<td></td>
<td>(0.1912)</td>
</tr>
<tr>
<td>$f_{a}$</td>
<td>0.0321</td>
</tr>
<tr>
<td></td>
<td>(0.0316)</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>-0.0029</td>
</tr>
<tr>
<td>$f_{a}$</td>
<td>-0.0191</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>0.0496</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>0.0099</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>-0.0022</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>0.0198</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>0.0037</td>
</tr>
<tr>
<td>$f_{s}$</td>
<td>-0.0018</td>
</tr>
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Contd. (Table II)
TABLE II Contd.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>$f_{\alpha}$</td>
<td>0.0692</td>
<td>0.0681</td>
<td>0.0626</td>
</tr>
<tr>
<td>(0.065)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{R\alpha}-f_{R\beta}$</td>
<td>-0.0231</td>
<td>-0.0211</td>
<td>-0.0218</td>
</tr>
<tr>
<td>$f_{D\alpha}-f_{D\beta}$</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0006</td>
</tr>
<tr>
<td>$f_{\beta}-2f_{\alpha}$</td>
<td>-0.2867</td>
<td>-0.2868</td>
<td>-0.2816</td>
</tr>
<tr>
<td>$f_{\alpha,\beta}$</td>
<td>0.0857</td>
<td>0.0826</td>
<td>0.0624</td>
</tr>
<tr>
<td>$3f_{\alpha}-3f_{\beta}$</td>
<td>0.3312</td>
<td>0.3586</td>
<td>0.2813</td>
</tr>
<tr>
<td>$3f_{\beta}-3f_{\alpha}$</td>
<td>1.1977</td>
<td>0.1811</td>
<td>0.1922</td>
</tr>
<tr>
<td>$f_{r\gamma}$</td>
<td>0.0019</td>
<td>0.0011</td>
<td>0.0012</td>
</tr>
<tr>
<td>$f_{r\theta}$</td>
<td>-0.1098</td>
<td>-0.1028</td>
<td>-0.1021</td>
</tr>
<tr>
<td>$f_{r\phi}$</td>
<td>-0.2061</td>
<td>-0.3076</td>
<td>-0.2214</td>
</tr>
</tbody>
</table>

*Values in the parenthesis refer to Imai et al. values.**

(1) The values obtained for the C ≡ C bond stretching force constant ($f_D$) for all the molecules is reasonable and the values are in agreement with the triple bond character between the carbon atoms.

(2) The statement *"Since the isotopic molecules have the same electronic structure, the potential function under the influence of which the nuclei are moving is the same to a very high degree of approximation"* by Herzberg** is certainly reflected in the unique sets of values obtained here for the three sets of isotopic molecules.

(3) The C-H bond force constants $f_i$ assume higher value than the $f_r$ force constants in all the molecules. This may be attributed to the influence of Hg on $f_r$ constants.

(4) The interaction force constants $f_{r r}, f_{r R}, f_{r D}, f_{R D}, f_{R r}, f_{D D}, f_{D t}, f_{t r}, f_{\alpha \beta}, f_{\alpha \gamma}, f_{\beta \delta}, f_{\phi}, (f_{R\alpha} - f_{R\beta}), (f_{D\alpha} - f_{D\beta})$ are uniquely negative in all the cases.

(5) Of all the interaction force constants $f_r$, assumes high value in all the cases. It has been shown** that the stretch-stretch interaction force constant of a triatomic molecule has a large positive value, if the bonding is highly delocalized and a negative value if the bonds are highly localised. Hence, the sign of the force constant is a measure of the electron localization or delocalization in a molecule.

(6) Hg-CCH bond force constants in all the cases agree quite well with the similar bonds in CH$_3$HgCN, SiH$_3$CCH, SiH$_2$CN, GeH$_3$CCH and GeH$_3$CCN molecules** (CCH group is isoelectronic with the CN).

(7) The major force constants evaluated in the present work compares well with Imai et al.** The force constants reported in the present work reproduces the observed wave numbers fairly well.

The vibrational mean amplitudes for both the bonded and non-bonded distances and the shrinkage at 298.16 K are reported in Tables III and IV respectively. All the bonded and non-bonded mean amplitudes are the same for the isotopic molecules CH$_3$HgCCH, CH$_3$HgCCD, CD$_3$HgCCH and CD$_3$HgCCD. The
Table III

Mean amplitudes (10^4Å) at 298.16 K

<table>
<thead>
<tr>
<th>Designation with atom number</th>
<th>CH₃HgCCH</th>
<th>CH₃HgCCD</th>
<th>CD₃HgCCH</th>
<th>CD₃HgCCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>l₁ (4–3)</td>
<td>7.9865</td>
<td>7.8126</td>
<td>7.9958</td>
<td>8.1265</td>
</tr>
<tr>
<td>l₁ (5–4)</td>
<td>5.1216</td>
<td>5.1211</td>
<td>5.7261</td>
<td>5.7265</td>
</tr>
<tr>
<td>l₄ (6–5)</td>
<td>4.8216</td>
<td>4.8164</td>
<td>4.8105</td>
<td>4.7126</td>
</tr>
<tr>
<td>l₅ (7–6)</td>
<td>3.8124</td>
<td>3.9111</td>
<td>3.9105</td>
<td>3.8792</td>
</tr>
<tr>
<td>l₆ (8–7)</td>
<td>7.4625</td>
<td>7.8642</td>
<td>7.5421</td>
<td>7.6546</td>
</tr>
<tr>
<td>l₁H₁H₁ (1–3)</td>
<td>13.1102</td>
<td>13.1911</td>
<td>13.8103</td>
<td>13.5102</td>
</tr>
<tr>
<td>l₁H₁H₁ (1–5)</td>
<td>12.0969</td>
<td>12.5126</td>
<td>12.7217</td>
<td>12.1276</td>
</tr>
<tr>
<td>l₁H₁C₁ (1–6)</td>
<td>14.8726</td>
<td>15.0121</td>
<td>14.9889</td>
<td>14.9217</td>
</tr>
<tr>
<td>l₁H₁H₁ (1–8)</td>
<td>20.6124</td>
<td>20.8195</td>
<td>21.1211</td>
<td>20.6982</td>
</tr>
</tbody>
</table>

Table IV

Shrinkage constants (Å) at 298.16 K

<table>
<thead>
<tr>
<th></th>
<th>CH₃HgCCH</th>
<th>CH₃HgCCD</th>
<th>CD₃HgCCH</th>
<th>CD₃HgCCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>δC₁–C (4–6)</td>
<td>0.0033</td>
<td>0.0034</td>
<td>0.0034</td>
<td>0.0036</td>
</tr>
<tr>
<td>δC₁–C (4–7)</td>
<td>0.0101</td>
<td>0.0180</td>
<td>0.0111</td>
<td>0.0109</td>
</tr>
<tr>
<td>δC₁–H (4–8)</td>
<td>0.0212</td>
<td>0.0186</td>
<td>0.0218</td>
<td>0.0191</td>
</tr>
<tr>
<td>δH₁C (5–7)</td>
<td>0.0042</td>
<td>0.0045</td>
<td>0.0048</td>
<td>0.0049</td>
</tr>
<tr>
<td>δH₁C (5–8)</td>
<td>0.0187</td>
<td>0.0165</td>
<td>0.0189</td>
<td>0.0169</td>
</tr>
<tr>
<td>δC₁–H (6–8)</td>
<td>0.0126</td>
<td>0.0099</td>
<td>0.0131</td>
<td>0.0094</td>
</tr>
</tbody>
</table>

High value force constants C= C yield small mean amplitude value for the corresponding bond. C–H bond mean amplitudes possess large value due to the low mass of H₂ atom. The values of C= C and C–H bond mean amplitudes compare well with the corresponding bonds in other molecules available in the literature favourably. The present values for shrinkage constants are in the expected range.

The Coriolis vibration rotation constants and the rotational distortion constants of the molecules under study are reported in Tables V and VI respectively. The high values of constants ζ₁₈, ζ₁₉, ζ₁₁₁₁, ζ₁₂₁₂, ζ₂₉ and ζ₄₇ suggest heavy mixing of the corresponding vibrational modes. The ζ values are found to obey the following sum rule for the E × E coupling

\[ \zeta^2_7 + \zeta^2_8 + \zeta^2_9 + \zeta^2_{7/10} + \zeta^2_{7/11} + \zeta^2_{7/12} = 1 \]

These coefficients give a measure of the extension of the infrared band contours. ζχ and ζη values of the A₁ × E coupling have the same magnitude which arises from the symmetry of these molecules.
**Table V**

_Coriolis coupling constants_

<table>
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<tr>
<th></th>
<th>CH₃HgCCH</th>
<th>CH₃HgCCD</th>
<th>CD₃HgCCH</th>
<th>CD₃HgCCD</th>
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<td>0.0019</td>
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<tr>
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<td>0.0001</td>
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<td>0.0085</td>
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<td>0.0499</td>
<td>0.0388</td>
<td>0.0511</td>
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</table>

*(Contd. Table V)*
\[ \zeta_{1,13} \quad 0.1899 \quad 0.1978 \quad 0.1811 \quad 0.1805 \]
\[ \zeta_{6,7} \quad 0.5712 \quad 0.5756 \quad 0.5972 \quad 0.6012 \]
\[ \zeta_{5,8} \quad 0.4128 \quad 0.5168 \quad 0.5926 \quad 0.6421 \]
\[ \zeta_{5,10} \quad 0.4077 \quad 0.5099 \quad 0.3098 \quad 0.6107 \]
\[ \zeta_{6,10} \quad 0.1561 \quad 0.1671 \quad 0.1921 \quad 0.1213 \]
\[ \zeta_{6,11} \quad 0.1956 \quad 0.1988 \quad 0.2021 \quad 0.1817 \]
\[ \zeta_{7,13} \quad 0.8821 \quad 0.8567 \quad 0.9010 \quad 0.9516 \]
\[ \zeta_{7,17} \quad 0.1742 \quad 0.1927 \quad 0.1817 \quad 0.1925 \]
\[ \zeta_{8,8} \quad 0.1211 \quad 0.1210 \quad 0.1214 \quad 0.1568 \]
\[ \zeta_{8,9} \quad 0.1064 \quad 0.1125 \quad 0.1086 \quad 0.1081 \]
\[ \zeta_{9,10} \quad 0.4471 \quad 0.4378 \quad 0.5817 \quad 0.4128 \]
\[ \zeta_{9,11} \quad 0.2423 \quad 0.2811 \quad 0.1818 \quad 0.2561 \]
\[ \zeta_{10,12} \quad 0.2198 \quad 0.2971 \quad 0.3011 \quad 0.4181 \]

**Table VI**

*Rotational distortion constants (KHz)*

<table>
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<tr>
<th></th>
<th>CH\textsubscript{3}HgCCH</th>
<th>CH\textsubscript{3}HgCCD</th>
<th>CD\textsubscript{3}HgCCH</th>
<th>CD\textsubscript{2}HgCCD</th>
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<td>(D_J)</td>
<td>15.2561</td>
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<td>9.7657</td>
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<td>(D_{JK})</td>
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<td>(D_K)</td>
<td>141.1125</td>
<td>129.8928</td>
<td>104.5165</td>
<td>84.6213</td>
</tr>
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</table>

The rotational distortion constant \(D_J\) in

(i) CH\textsubscript{3}HgCCH \(>\) CH\textsubscript{3}HgCCD

and

(ii) CD\textsubscript{3}HgCCH \(>\) CD\textsubscript{2}HgCCD

This is due to the difference in mass of the molecule. Further the positive value for \(D_J\) indicates that the centrifugal force about any given axis will always tend to increase the moment of inertia about that axis, which in turn reduce the centrifugal distortion constants. In general, the magnitude of the centrifugal distortion constant decrease with the increase of the mass of the molecule.

**Conclusions**

The kinetic constants and certain simplifying considerations are used in evaluating the molecular constants. It may be seen that highly systematic and reasonable sets of molecular constants relating to methylthynylmercury and its isotopes are available for the first time. The potential constants evaluated in the present investigation are found to be very interesting from the point of view of molecular dynamics. The method of using kinetic constants in evaluating the potential constants appear to be fruitful in simple cases as well as the present complicated molecular type. The evaluated potential constants are utilised in evaluating reasonable mean amplitudes, shrinkage constants, Coriolis coupling constants and centrifugal distortion constants.
ACKNOWLEDGEMENT

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