# The Rotational Wave Equation of Tetramethylmethane for Zero Potential and a Generalization 

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#### Abstract

An exact solution for the rotational wave equation of tetramethylmethane for constant potential has been found. The solution is very similar to that of the rigid spherical top, which is the other limiting case for the rotational motion of the molecule in question. The energy levels for free rotation of the methyl groups are spread out compared to those for fixed methyl groups. This might make possible an estimation of the potential function between


the groups. The energy levels might be used to calculate the specific heat. Some selection rules are given for infrared and Raman spectra although the rotational spectra are just beyond the limit of resolution at present. A generalization has been made for a spherical top with attached gyroscopes whose axes are rigidly fixed on the top according to certain symmetry requirements.

## I. Introduction

$\mathrm{C}^{o}$ONSIDERABLE quantum-mechanical work has been done on the symmetrical top ${ }^{1}$ and Nielsen ${ }^{2}$ has treated a generalization in which there is a degree of torsional freedom between two principal parts of the rotator about an axis of symmetry. The present paper gives an
exact solution for the spherical top with tetrahedrally spaced gyroscopes of equal moments of inertia. This wave equation is of interest because it becomes the rotational wave equation for tetramethylmethane, $\mathrm{C}\left(\mathrm{CH}_{3}\right)_{4}$, if a suitable potential function is added.

## II. Solution of the Wave Equation

The five C atoms of tetramethylmethane, one at the center and four at the corners of a regular tetrahedron, are equivalent to a spherical top. The C atoms at the corners are the C atoms of four methyl groups each of which can rotate about a line through its $C$ atom and the center atom. The methyl groups are equivalent to the tetrahedrally spaced gyroscopes.

The coordinates used are as follows. The angles $\alpha_{1}, \alpha_{2}, \alpha_{3}$, and $\alpha_{4}$ give the positions of the gyroscopes, or methyl groups, with respect to the $\mathrm{C}_{5}$ tetrahedron. The angles $\theta, \varphi$ and $\chi$ are Eulerian angles giving the orientation of the tetrahedron. The axes $x_{0}, y_{0}, z_{0}$ in Fig. 1 are fixed in space while the axes $x, y, z$ are fixed on the $\mathrm{C}_{5}$ tetrahedron. $\theta$ is the angle between the $z_{0}$ and $z$ axes, and $\varphi$ and $\chi$ are, respectively, the angles between the line of nodes and the $x$ and $x_{0}$ axes.

The kinetic energy $T$ is given in terms of the angular velocities by the expression

$$
\begin{align*}
& 2 T=I\left\{\dot{\chi}^{2}+2 \cos \theta \dot{\chi} \dot{\varphi}+\dot{\varphi}^{2}+\dot{\theta}^{2}\right\}+\sum_{k=1}^{4} I_{s}\left\{\left[\left(Q_{y k} \sin \varphi-Q_{x k} \cos \varphi\right) \sin \theta+Q_{z k} \cos \theta\right] 2 \dot{\chi} \dot{\alpha}_{k}\right. \\
&\left.+\left[Q_{y k} \cos \varphi+Q_{x k} \sin \varphi\right] 2 \dot{\theta} \dot{\alpha}_{k}+2 Q_{z k} \dot{\chi} \dot{\alpha}_{k}+\dot{\alpha}_{k}^{2}\right\} \tag{1}
\end{align*}
$$

when $I=$ moment of inertia of the whole molecule with the methyl groups fixed, $I_{s}=$ moment of inertia of a methyl group about its axis of symmetry, and $Q_{x k}, Q_{y k}$ and $Q_{z k}=$ direction cosines on the previously described $x, y$ and $z$ axes of the axis of rotation of the $k$ th methyl group.

The kinetic energy in terms of the momenta is given by
$2 T=\frac{1}{I_{0}}\left\{p_{\theta}{ }^{2}+\frac{p_{\chi}^{2}}{\sin ^{2} \theta}-\frac{2 p_{\varphi} p_{\chi} \cos \theta}{\sin ^{2} \theta}+\frac{p_{\varphi}{ }^{2}}{\sin ^{2} \theta}-\frac{2 p_{\chi}}{\sin \theta} \sum_{k=1}^{4}\left(Q_{y l k} \sin \varphi-Q_{x k} \cos \varphi\right) p_{\alpha_{k}}\right.$

[^0]\[

$$
\begin{align*}
&-2 p_{\theta} \sum_{k=1}^{4}\left(Q_{y k} \cos \varphi+Q_{x k} \sin \varphi\right) p_{\alpha_{k}}-2 p_{\varphi}\left[\sum_{k=1}^{4} Q_{z k}-\frac{\cos \theta}{\sin \theta} \sum_{k=1}^{4}\left(Q_{y k} \sin \varphi-Q_{x k} \cos \varphi\right)\right] p \alpha_{k} \\
&\left.+\sum_{k=1}^{4} \frac{I_{0}}{I_{s}} p_{\alpha_{k}}{ }^{2}+\sum_{k, l=1}^{4} p \alpha_{k} p_{\alpha_{l}} \cos k l\right\} \tag{2}
\end{align*}
$$
\]

where $I_{0}=I-(4 / 3) I_{s}$ and $\cos k l=$ the cosine of the angle between the axes of the $k$ th and $l$ th methyl groups.

The wave equation was obtained by the method given by Schrödinger. ${ }^{3}$ It is

$$
\begin{align*}
& \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \Psi}{\partial \theta}\right)-2 \sin \theta \sum_{k=1}^{4}\left(Q_{y k} \cos \varphi+Q_{x k} \sin \varphi\right) \frac{\partial^{2} \Psi}{\partial \theta \partial \alpha_{k}}+-\frac{1}{\sin \theta} \frac{\partial^{2} \Psi}{\partial \chi^{2}}-\frac{2 \cos \theta}{\sin \theta} \frac{\partial^{2} \Psi}{\partial \chi \partial \varphi} \\
& -2 \sum_{k=1}^{4}\left(Q_{y k} \sin \varphi-Q_{x k} \cos \varphi\right) \frac{\partial^{2} \Psi}{\partial \chi \partial \alpha_{k}}+\frac{1}{\sin \theta} \frac{\partial^{2} \Psi}{\partial \varphi^{2}}-2 \sin \theta \sum_{k=1}^{4} Q_{z k} \frac{\partial^{2} \Psi}{\partial \varphi \partial \alpha_{k}} \\
& \quad+2 \cos \theta \sum_{k=1}^{4}\left(Q_{y k} \sin \varphi-Q_{x k} \cos \varphi\right) \frac{\partial^{2} \Psi}{\partial \varphi \partial \alpha_{k}}+\sin \theta \sum_{k=1}^{4} \frac{I_{0}}{I_{s}} \frac{\partial^{2} \Psi}{\partial \alpha_{k}^{2}}+\sin \theta \sum_{k, l=1}^{4} \cos k l \frac{\partial^{2} \Psi}{\partial \alpha_{k} \partial \alpha_{l}} \\
& +\frac{8 \pi^{2} I_{0}}{h^{2}} \sin \theta(E-V) \Psi=0 \tag{3}
\end{align*}
$$

Only the case in which the potential is zero will be considered. For this case it can be seen from the wave equation that the $\alpha_{k}$ 's are cyclic variables. The wave function can therefore be taken as

$$
\begin{equation*}
\Psi\left(\theta, \varphi, \chi, \alpha_{1}, \alpha_{2}, \alpha_{3}, \alpha_{4}\right)=\psi(\theta, \varphi, \chi) \prod_{k=1}^{4} e^{i m_{k} \alpha_{k}} \tag{4}
\end{equation*}
$$

where the $m_{k}$ 's are integers because of the single-valuedness of $\Psi$. Substituting this wave function into the wave equation gives

$$
\begin{gather*}
\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta}\right)-2 i \sin \theta\left[\sum_{k=1}^{4} m_{k}\left(Q_{y k} \cos \varphi+Q_{x k} \sin \varphi\right)\right] \frac{\partial \psi}{\partial \theta}+\frac{1}{\sin \theta} \frac{\partial^{2} \psi}{\partial \chi^{2}}-\frac{2 \cos \theta}{\sin \theta} \frac{\partial^{2} \psi}{\partial \chi \partial \varphi} \\
-2 i\left[\sum_{k=1}^{4} m_{k}\left(Q_{y k} \sin \varphi-Q_{x k} \cos \varphi\right)\right] \frac{\partial \psi}{\partial \chi}+\frac{1}{\sin \theta} \frac{\partial^{2} \psi}{\partial \varphi^{2}}-2 i \sin \theta \sum_{k=1}^{4} m_{k} Q_{z k} \frac{\partial \psi}{\partial \varphi} \\
+2 i \cos \theta\left[\sum_{k=1}^{4} m_{k}\left(Q_{y k} \sin \varphi-Q_{x k} \cos \varphi\right)\right] \frac{\partial \psi}{\partial \varphi}-\sin \theta \sum_{k=1}^{4} \frac{I_{0}}{I_{s}} m_{k}^{2} \psi \\
-\sin \theta \sum_{k, l=1}^{4} \cos k l m_{k} m_{l} \psi+\frac{8 \pi^{2} I_{0}}{h^{2}} \sin \theta E \psi=0 \tag{5}
\end{gather*}
$$

It is possible to eliminate the terms in the preceding equation which involve $\varphi$ explicitly by properly choosing the $x, y, z$ axes with respect to the $C_{5}$ tetrahedron. These axes are fixed on the tetrahedron, but their orientation is arbitrary. The proper orientation for the elimination can be found as follows. Along the axes of rotation of the methyl groups consider momentum vectors whose

[^1]magnitudes are given by the corresponding quantum numbers $m_{k}$. Then the expressions $\sum^{4}{ }_{k=1} m_{k} Q_{x k}$, $\sum^{4}{ }_{k=1} m_{k} Q_{y k}$, and $\sum^{4}{ }_{k=1} m_{k} Q_{z k}$ are components along the $x, y$ and $z$ axes of the resultant momentum of the four methyl groups. For any given values of the $m_{k}$ 's it is always possible to choose the $x$, $y$ and $z$ axes in such a way that the resultant lies along the $z$-axis and therefore the $x$ and $y$ components are zero. This can be shown analytically as follows. Take any set of fixed axes $x^{\prime \prime}, y^{\prime \prime}, z^{\prime \prime}$ on the $\mathrm{C}_{5}$ tetrahedron. Rotate $\beta$ degrees about the $z^{\prime \prime}$-axis to get the new $x^{\prime}, y^{\prime}, z^{\prime}$ axes. Next rotate the primed axes $\delta$ degrees about the $y^{\prime}$ axis to get the $x, y, z$ axes. Then the $y$ and $x$ components of the resultant momentum of the methyl groups are, respectively
\[

$$
\begin{equation*}
\sum_{k=1}^{4} m_{k} Q_{y k}=K_{2} \sin \left(\beta-\beta_{0}\right) \tag{6}
\end{equation*}
$$

\]

and

$$
\begin{equation*}
\sum_{k=1}^{4} m_{k} Q_{x k}=\left[K_{3}{ }^{2}+K_{2}{ }^{2} \cos ^{2}\left(\beta-\beta_{0}\right)\right]^{\frac{1}{2}} \sin \left(\delta-\delta_{0}\right) \tag{7}
\end{equation*}
$$

where $K_{2}, K_{3}, \beta_{0}$, and $\delta_{0}$ depend only on the $m_{k}$ 's and are therefore constant for any particular choice of the $m_{k}$ 's. Taking $\beta=\beta_{0}$ and $\delta=\delta_{0}$ gives

$$
\begin{equation*}
\sum_{k=1}^{4} m_{k} Q_{y k}=0 \tag{8}
\end{equation*}
$$

$$
\begin{equation*}
\sum_{k=1}^{4} m_{k} Q_{x k}=0 \tag{9}
\end{equation*}
$$

and

$$
\begin{equation*}
\sum_{k=1}^{4} m_{k} Q_{z k}=\left(\sum_{k, l=1}^{4} \cos k l m_{k} m_{l}\right)^{\frac{1}{2}}=\text { the resultant momentum of the four methyl groups. } \tag{10}
\end{equation*}
$$

Define

$$
\begin{equation*}
Q=\left(\sum_{k, l=1}^{4} \cos k l m_{k} m_{l}\right)^{\frac{1}{2}} \tag{11}
\end{equation*}
$$

Then the wave equation becomes

$$
\begin{align*}
& \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \psi}{\partial \theta}\right)+\frac{1}{\sin \theta} \frac{\partial^{2} \psi}{\partial \chi^{2}}-\frac{2 \cos \theta}{\sin \theta} \frac{\partial^{2} \psi}{\partial \chi \partial \varphi}+\frac{1}{\sin \theta} \frac{\partial^{2} \psi}{\partial \varphi^{2}}-2 i \sin \theta Q \frac{\partial \psi}{\partial \varphi}-\sin \theta \sum_{k=1}^{4} \frac{I_{0}}{I_{s}} m_{k}{ }^{2} \psi \\
&-\sin \theta Q^{2} \psi+\frac{8 \pi^{2} I_{0}}{h^{2}} \sin \theta E \psi=0 \tag{12}
\end{align*}
$$

Since $\chi$ and $\varphi$ are cyclic, $\psi$ may be taken as

$$
\begin{equation*}
\psi(\theta, \varphi, \chi)=\Theta(\theta) e^{i m_{\varphi} \varphi} e^{i m_{\chi} \chi} \tag{13}
\end{equation*}
$$

where $m_{\chi}$ and $m_{\varphi}$ are integers because of the single-valuedness of $\Psi$. Substituting this value of $\psi$ into the wave equation gives

$$
\begin{equation*}
\sin \theta \frac{d}{d \theta}\left(\sin \theta \frac{d \Theta}{d \theta}\right)-\left[m_{\chi}^{2}+m_{\varphi}^{2}-2 m_{\chi} m_{\varphi} \cos \theta+\left(\sum_{k=1}^{4} \frac{I_{0}}{I_{s}} m_{k}^{2}+Q^{2}-2 Q m_{\varphi}-\frac{8 \pi^{2} I_{0}}{h^{2}} E\right) \sin ^{2} \theta\right] \Theta=0 \tag{14}
\end{equation*}
$$

Let

$$
\begin{equation*}
\lambda=\left(8 \pi^{2} I_{0} / h^{2}\right) E-\sum_{k=1}^{4}\left(I_{0} / I_{s}\right) m_{k}^{2}-Q^{2}+2 Q m_{\varphi} \tag{15}
\end{equation*}
$$

Then the wave equation becomes identical with the wave equation for the symmetrical top. ${ }^{4}$ The

[^2]function $\Theta(\theta)$ involves Jacobian polynomials; an expression is given for it later. The energy levels are given by the formula
\[

$$
\begin{equation*}
E=\left(h^{2} / 8 \pi^{2} I_{0}\right)\left\{j(j+1)+\sum_{k=1}^{4}\left(I_{0} / I_{s}\right) m_{k}^{2}+Q^{2}-2 Q m_{\varphi}\right\}, \tag{16}
\end{equation*}
$$

\]

where the total quantum number $j$ is an integer equal to or greater than the larger of the two quantities $\left|m_{\varphi}\right|$ and $\left|m_{\chi}\right|$, and $Q$ is the vector sum of the momenta of the methyl groups as given by Eq. (11).

## III. Selection Rules

It has been mentioned that the $\varphi$-axis was taken in the direction of the resultant momentum of the methyl groups in order to separate the variables. It will now be shown that selection rules for $j, m_{\varphi}$, and $m_{\chi}$ can be obtained for transitions in which it is not necessary to shift the $\varphi$-axis, or in other words for transitions in which the direction of the resultant momentum of the methyl groups is not changed with respect to the $C_{5}$ tetrahedron. If no interaction between vibration and rotation is assumed, then the wave function can be written as

$$
\begin{equation*}
\Psi\left(\theta, \chi, \varphi, \alpha_{1}, \cdots \alpha_{4}, \xi_{1}, \cdots \xi_{n}\right)=\psi(\theta, \chi, \varphi) e^{i m_{1} \alpha_{1} \cdots} \cdots e^{i m_{4} \alpha_{4}} H_{1}\left(\xi_{1}\right) \cdots H_{n}\left(\xi_{n}\right) \tag{17}
\end{equation*}
$$

when the $\xi_{k}$ 's are normal coordinates of vibration, and the $H_{k}\left(\xi_{k}\right)$ 's are the corresponding eigenfunctions.

Let $M_{i}$ and $\beta_{i k}$ be, respectively, the electric moment and polarization for axes fixed in space and $M_{i^{\prime}}$ and $\beta_{i^{\prime} k^{\prime}}$ the moment and polarization for axes fixed on the sphere. Then

$$
\begin{equation*}
M_{i}=\sum_{i^{\prime}} M_{i^{\prime}} \cos i i^{\prime} \quad \text { (18) and } \quad \beta_{i k}=\sum_{i^{\prime}, k^{\prime}} \beta_{i^{\prime} k^{\prime}} \cos i i^{\prime} \cos k k^{\prime} \tag{19}
\end{equation*}
$$

when $\cos i i^{\prime}$ is the cosine of the angle between the $i$ and $i^{\prime}$ axes. It can be seen that $M_{i^{\prime}}$ and $\beta_{i^{\prime} k^{\prime}}$ depend on the $\alpha_{k}$ 's and $\xi_{k}$ 's, and the quantum numbers $m_{1}, m_{2}, m_{3}$ and $m_{4}$, which determine the direction of the $\varphi$-axis, while the functions $\cos i i^{\prime}$ depend only on $\theta, \chi$, and $\varphi$. The matrix elements for the infrared and Raman transition probabilities can therefore be written as

$$
\begin{equation*}
\left(M_{i}\right)_{V^{\prime}, m_{1}^{\prime}, \cdots m_{4^{\prime}}, j^{\prime}, m^{\prime} \varphi, m^{\prime} x}^{V, m_{1}, \cdots m_{4}, j, m_{\varphi}, m_{x}}=\sum_{i^{\prime}}\left(M_{i^{\prime}}\right)_{V^{\prime}, m_{1}, \cdots m_{4^{\prime}}}^{V, m_{1}, \cdots m_{4}}\left(\cos i i^{\prime}\right)_{j^{\prime}, m^{\prime} \varphi, m^{\prime} x}^{j, m_{\varphi}, m x} \tag{20}
\end{equation*}
$$

and

$$
\begin{equation*}
\left(\beta_{i k}\right)_{V^{\prime}, m_{1}^{\prime}, \cdots m_{4^{\prime}}, j^{\prime}, m^{\prime} \varphi, m^{\prime} \chi}^{V, m_{1}, \cdots m_{4}, j, m_{\varphi}, m_{\chi}}=\sum_{i^{\prime} k^{\prime}}\left(\beta_{i^{\prime} k^{\prime}}\right)_{V^{\prime}, m_{1^{\prime}}, \cdots m_{4^{\prime}}}^{V, m_{1}, \cdots m_{4}}\left(\cos i i^{\prime} \cos k k^{\prime}\right)_{j^{\prime}, m_{\varphi}^{\prime} \varphi, m^{\prime} \chi}^{j, m_{\varphi}, m_{\chi}} \tag{21}
\end{equation*}
$$

when $V$ and $V^{\prime}$ represent the totality of vibration quantum numbers. It will be seen that the matrix elements $\left(\cos i i^{\prime}\right)_{j^{\prime}, m_{\varphi}^{\prime} \varphi, m^{\prime} x}^{j, m_{\varphi}, m \chi}$ and $\left(\cos i i^{\prime} \cos k k^{\prime}\right)_{j^{\prime}, m_{\varphi}^{\prime} \varphi, m \chi^{\prime}}^{j, m_{\varphi}, m \chi}$ are the same as those occurring in the corresponding matrices for the symmetrical top. The selection rules for this case are therefore as follows. For infrared transitions $\Delta j, \Delta m_{\varphi}$ and $\Delta m_{\chi}$ can have the values 0 or $\pm 1$, while for Raman transitions they can have the values $0, \pm 1$, or $\pm 2$.

A rough idea of the selection rules for the methyl group quantum numbers can be obtained as follows. Consider classically, first, vibrations of the $H$ atoms of a single methyl group, the C atoms being assumed fixed, and second, vibrations of the C atoms, the $H$ atoms being assumed rigidly fixed to them. The forces and masses involved in these two classes of vibrations show that the frequencies of the two classes differ considerably. It follows that the normal coordinates of vibration of the tetramethylmethane molecule can be divided into two classes with the following properties. Each normal coordinate in the first class depends almost entirely on the coordinates of the $H$ atoms of a single methyl group while the normal coordinates in the second class depend almost entirely on the coordinates of the C atoms. Designate the quantum numbers of the first class by $V_{1}$ and $V_{1}^{\prime}$ and those of the second class by $V_{2}$ and $V_{2}{ }^{\prime}$.

Let the assumption now be made that the electric moment $M_{i^{\prime}}$ and the polarizability $\beta_{i^{\prime} k^{\prime}}$ with respect to the $\mathrm{C}_{5}$ tetrahedron can be expressed as follows

$$
\begin{equation*}
M_{i^{\prime}}=M_{i^{\prime}}^{(c)}+\sum_{l} M_{i^{\prime}}^{(l)} \tag{22}
\end{equation*}
$$

$$
\begin{equation*}
\text { and } \quad \beta_{i^{\prime} k^{\prime}}=\beta_{i^{\prime} k^{\prime}}(c)+\sum_{l} \beta_{i^{\prime} k^{\prime}}(l) \tag{23}
\end{equation*}
$$

where the first term on the right in both expressions depends only on the coordinates of the C atoms, and $M_{i^{\prime}}{ }^{(l)}$ and $\beta_{i^{\prime} k^{\prime}}{ }^{(l)}$ depend only on the coordinates of the $H$ atoms in the $l$ th methyl group. The remainder of the argument will be carried out only for the electric moment; it can be applied equally well to the polarizability. Let $M_{i^{\prime \prime} \iota}$ represent the moment of the $H$ atoms of the $l$ th methyl group with respect to axes fixed on this methyl group. Then Eq. (22) becomes

$$
\begin{equation*}
M_{i^{\prime}}=M_{i^{\prime}}{ }^{(c)}+\sum_{l, i^{\prime \prime} l} M_{i^{\prime \prime} l} \cos i^{\prime} i^{\prime \prime}{ }_{l} \tag{24}
\end{equation*}
$$

when $\cos i^{\prime} i^{\prime \prime}{ }_{l}$ represents the cosine of the angle between the $i^{\prime}$ axis and the $i^{\prime \prime}{ }_{l}$ axis on the $l$ th methyl group. The matrix element can then be expressed as

$$
\begin{equation*}
\left.\left(M_{i}\right)_{j^{\prime}, m_{\varphi^{\prime}}, m^{\prime} \chi, V_{1^{\prime}}, V_{2^{\prime}, m_{1^{\prime}}, \cdots m_{4^{\prime}}}^{j, m_{\chi}, V_{1}, V_{2}, m_{1}, \cdots m_{4}}=\sum_{i^{\prime}}\left(\cos i i^{\prime}\right)_{j^{\prime}, m_{\varphi^{\prime}}, m^{\prime} x}^{j, m_{\varphi}, m_{\chi}}\left(\left(M_{i^{\prime}}\right)_{V_{1^{\prime}}, m_{1^{\prime}}, \cdots m_{4^{\prime}}}^{V_{1}, m_{1}, \cdots m_{4}}\right.}^{V_{2}}\right)_{V_{2^{\prime}}}^{V_{2}} \tag{25}
\end{equation*}
$$

when

$$
\begin{align*}
\left.\left(M_{i^{\prime}}\right)\right)_{V_{1}^{\prime}, m_{1}^{\prime}}^{V_{1}, m_{1}, \cdots m_{4^{\prime}}}=\left(M_{i^{\prime}}(c)\right)_{V_{1^{\prime}}}^{V_{1}} \int & e^{i\left(m_{1}-m_{1^{\prime}}^{\prime}\right) \alpha_{1}} \cdots e^{i\left(m_{4}-m_{4^{\prime}}\right) \alpha_{4}} d \alpha_{1} \cdots d \alpha_{4} \\
& \quad+\sum_{l, i_{l}^{\prime \prime}}\left(M_{i^{\prime}}\right)_{V_{1^{\prime}}}^{V_{1}} \int \cos i^{\prime} i_{l}^{\prime \prime} e^{i\left(m_{1}-m_{1^{\prime}}\right) \alpha_{1}} \cdots e^{i\left(m_{4}-m_{4^{\prime}}\right) \alpha_{4}} d \alpha_{1} \cdots d \alpha_{4} \tag{26}
\end{align*}
$$

The first integral is zero unless all the $m_{k}$ 's do not change, while the parts of the other integrals involving $\alpha_{l}$ are the same as those occurring in the case of the rotator. The selection rules therefore become $\Delta m_{k}=0, \pm 1$ for infrared transitions. A similar treatment gives $\Delta m_{k}=0, \pm 1, \pm 2$ for Raman transitions. It also follows from Eq. (26) that two $m_{k}$ 's cannot change simultaneously; this is a result of the assumed independence of the electric moment and polarization of the methyl groups. Since this assumption is not strictly true, the selection rules obtained for the $m_{k}$ 's are only approximate.

## IV. Discussion of Wave Functions, Energy Levels, and Selection Rules

In summing up it may be said that the Eulerian angle $\chi$ and the four angles $\alpha_{k}$ giving the positions of the methyl groups were cyclic. The Eulerian angle $\varphi$ was made cyclic by taking the $\varphi$-axis in the direction of the resultant momentum of the methyl groups. This gave the following wave function

$$
\begin{equation*}
\Psi\left(\theta, \chi, \varphi, \alpha_{1}, \alpha_{2}, \alpha_{3}, \alpha_{4}\right)=\Theta(\theta) e^{i m_{\chi}} \chi e^{i m_{\varphi} \varphi} e^{i m_{1} \alpha_{1}} e^{i m_{2} \alpha_{2}} e^{i m_{3} \alpha_{3}} e^{i m_{4} \alpha_{4}}, \tag{27}
\end{equation*}
$$

where the quantum numbers are all integers because of the single-valuedness of $\Psi$. The differential equation obtained for $\Theta(\theta)$ is the well-known one obtained in the case of the symmetrical top. The function $\Theta(\theta)$ is a polynomial of the $l$ th degree in $\cos \theta$ and has the form

$$
\begin{equation*}
\Theta_{l}{ }^{\left(m_{\varphi}\right)\left(m_{\chi}\right)}(\theta)=(1-x)^{\left|m_{\varphi}-m \chi\right| / 2}(1+x)^{\left|m_{\varphi}+m_{\chi}\right| / 2} G_{l-m^{*}}(p, q, x), \tag{28}
\end{equation*}
$$

when

$$
\begin{gather*}
m^{*}=\left(\left|m_{\varphi}-m_{\chi}\right|+\left|m_{\varphi}+m_{\chi}\right|\right) / 2,  \tag{29}\\
G_{l-m^{*}}(p, q, x)=\frac{x^{1-q}(1-x)^{q-p}}{q(q+1) \cdots\left(q+l-m^{*}-1\right)} \frac{d^{l-m^{*}}}{d x^{l-m^{*}}}\left[x^{q+l-m^{*-1}}(1-x)^{p+l-m^{*}-q}\right],  \tag{30}\\
q=1+\left|m_{\varphi}+m_{\chi}\right|, \quad \text { (31) } \quad p=2 m^{*}+1 \quad \text { (32) and } \quad x=(1+\cos \theta) / 2 \tag{33}
\end{gather*}
$$

The function $G_{l-m^{*}}(p, q, x)$ is the $l-m$ th Jacobian polynomial in $x$.


Fig. 1. Eulerian angles.

The energy levels are given by Eq. (16). A diagram of the lower levels is given in Fig. 2 where the lower levels are also given for a molecule of tetramethylmethane with the methyl groups assumed fixed, which is the limiting case of the rotational motion for low temperatures. It can be seen from Fig. 2 that the six lowest energy levels for the two cases nearly coincide. They do not coincide exactly because the moment of inertia of a molecule with free methyl groups is slightly less than it would be if the methyl groups were fixed. This can be seen from the following classical consideration. Consider a torque applied to the molecule about one of its methyl group axes. This methyl group will not have to be accelerated, and therefore a greater acceleration will be given to the rest of the molecule than would be the case if the methyl groups were fixed.

The energy levels above the sixth are spread out compared to those for the rigid spherical top. This is caused by removal of the degeneracy in $m_{\varphi}$ in levels above the sixth. The energy levels might be used in calculating the specific heat, and the spreading out of the levels for the case of free rotation might make possible an estimation of the potential function between the methyl groups.

Although the rotational spectra of tetramethylmethane are at present just beyond the limit of resolution, the selection rules may be of value later. For transitions in which the direction
of the resultant momentum of the methyl groups remains the same with respect to the $\mathrm{C}_{5}$ tetrahedron, the selection rules are the same as for a symmetrical top, namely, $\Delta j, \Delta m_{\varphi}$ and $\Delta m_{\chi}$ can have the values 0 or $\pm 1$ for infrared transitions and the values $0, \pm 1$, or $\pm 2$ for Raman transitions. In transitions of the methyl group quantum numbers which involve a shift in the $\varphi$-axis, the selection rules for $j, m_{\varphi}$, and $m_{\chi}$ are probably much less sharp because the $\varphi$-axis is shifted in a rather arbitrary manner. Approximate selection rules were obtained for the methyl group quantum numbers by assuming that the interaction of H atoms in different methyl groups did not affect the electric moment or polarization. These approximate selection rules indicate that the stronger lines probably occur for infrared transitions in which $\Delta m_{k}=0$ or $\pm 1$ and for Raman transitions in which $\Delta m_{k}=0, \pm 1$, or $\pm 2$.


Fig. 2. Energy levels.

## V. Generalization

It has been found possible to generalize the conditions for which a wave equation analogous to Eq. (3) applies. Consider a rigid body with gyroscopes attached to it in such a way that the axes of the gyroscopes pass through the center
of gravity of the combination, the axes being fixed on the rigid frame. Assume the following three conditions to be fulfilled.
(I) The combination of the rigid frame and gyroscopes is a spherical top for all values of the coordinates giving the positions of the gyroscopes.
(II) Each of the gyroscopes is a symmetrical top which rotates about its unique axis through its center of gravity.
(III) The axes of the gyroscopes are placed in such a way that

$$
\sum_{k=1}^{n} I_{k} Q_{k}{ }^{2}=K_{1},
$$

when $I_{k}=$ the moment of inertia of the $k$ th gyroscope about its axis, $Q_{k}=$ the direction cosine of the $k$ th gyroscope axis on an arbitrary axis $q$, $K_{1}=$ a constant for all axes $q$, and the sum extends over all the gyroscopes.

The only changes necessary to be made in the previously obtained expressions for the kinetic energy, the wave equations, and the energy levels are the following. The sums extend over all $n$ gyroscopes; the moment of inertia $I_{s}$ must be replaced by $I_{k}$; and $I_{0}$ becomes $I-K_{1}$.

In conclusion I wish to express my gratitude to Professor Linus Pauling for having suggested this problem and for having made many valuable contributions to it.

# The Effect of Concentration, Temperature and Wave-Length of Light upon the Verdet Constant of Cerous Chloride Solutions 

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#### Abstract

The Verdet constants of solutions of cerous chloride in water have been measured at concentrations varying from zero to an almost saturated solution. Measurements were made at temperatures from 10 to $45^{\circ} \mathrm{C}$ and for the wavelengths 5893, 5461 and 4481 A . The results are given in the form of curves showing the Verdet constant as a function of temperature and as a function of concentration.


THE magnetic rotation of the plane of polarization of light is particularly interesting in the case of solutions of cerium salts. These solutions, when fairly concentrated, cause a negative rotation (opposite the direction of flow of current producing the magnetic field) and solutions may be prepared which for any one temperature and wave-length produce zero rotation. Data on the Verdet constant of these materials are not found in any standard tables nor in the literature.

The Verdet constants of solutions of cerous chloride in water from zero concentration to an almost saturated solution have been measured at temperatures from $10^{\circ} \mathrm{C}$ to $45^{\circ} \mathrm{C}$ for three wave-lengths of light: The rotations were measured by means of a Schmidt and Haensch

Tabulated values of the concentration, density, index of refraction and Verdet constant of the solutions are also given. Attention is called to the point that the effect attributed by Allison and Condon to a time lag in the Faraday effect may have been due to a temperature change during the course of their observations.
"Lippich" half-shade polarimeter, which could be read to hundredths of a degree. The three light sources used were: (1) the mercury "Labarc" with Corning Didymium and G34-Y filters to transmit $\lambda 5460.7 \mathrm{~A}$; (2) a sodium arc with Jena filters OG-1 and VG-1 (each 2 mm ) to transmit the $D$ lines at $\lambda 5893$; (3) a spark between magnesium electrodes with Jena filters BG-4 plus GG-3 (each 2 mm ) to transmit the spark line at $\lambda 4481$. The spark was operated from a Thordarson spark transformer with a condenser across the secondary.

The liquid whose rotation was being measured was placed in a water jacketed cell ${ }^{1} 26.15 \mathrm{~cm}$

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