Theory of Phase Transitions in Solid Methanes. VII

—The Intermolecular Potential and the Crystalline Field—

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The interaction between methane molecules in the solid state is discussed under the assumption of the pairwise interatomic interaction. A formal expression for the intermolecular interaction is derived in a form reflecting both molecular orientations and molecular symmetry. The isotropic part of this expression is compared with the potentials obtained from the second virial coefficients. The anisotropic parts dependent on the orientations of both molecules are worked out and compared with the James-Keenan model. Furthermore, the crystalline fields are obtained which a methane molecule feels in rare gas matrices as well as in solid methane.

§ 1. Introduction

In a series of papers\(^1–5\) we have studied the phase transitions and molecular rotation in solid methanes. The discussions have been developed on the basis of the James-Keenan model,\(^3\) referred to as the J-K model hereafter, in which the relevant intermolecular interaction is assumed to be essentially an effective octopole-octopole interaction. Comparison of the results obtained with experiment has led us to the conclusion that the J-K model successfully works as the first approximation to solid methanes.

In the present paper we wish to throw new light on the J-K model through a study of the intermolecular potential of methane molecules. In order to avoid the difficulties inherent to the study of electronic structures of polyatomic molecules, we shall adopt a drastic approximation from the beginning. That is, the intermolecular potential is assumed to consist of contributions from every pair of constituent atoms of both molecules. As is well known, Bartell,\(^8\) Hendrickson\(^9\) and in particular Kitaigorodskii and his group\(^10,11\) have made extensive and careful studies of this approximate method, so that it is now regarded as a practical, and sometimes an only method for evaluating intermolecular forces with satisfactory reliability.

Balescu\(^12\) and more recently Stevens\(^13\) have already made some important contributions to the present problem. However, Balescu’s results involve non-trivial errors,\(^14\) and Stevens’ work is not developed to high-enough order to be applicable to our problem. In addition, both works take into account only the interaction between hydrogen atoms involved. In other words, not only the pre-
sence of carbon atoms in both molecules but also the electrostatic interactions are completely neglected; this is hard to be justified. A study from the same standpoint has also been done by Uryu and Hirota.\(^{15}\)

In the present paper we report a new approach which is an immediate application of the general theory of two-center expansion of an arbitrary function developed by Yamamoto and the present author\(^{16}\) in a previous paper. Section 2 is devoted to finding a complete expression for the intermolecular potential between two methane molecules in a form of a series expansion. The numerical values of the parameters which characterize the assumed interatomic interactions are estimated in §3 based on the works done by Bartell and others.\(^{8-11}\) The isotropic part is evaluated and compared with the result known from the second virial coefficient in §4. The anisotropic parts that depend on the orientations of both molecules are worked out in full detail in §5. It is shown there that in the solid state the largest term is indeed that which has the same form as an octopole-octopole interaction, but that the remaining terms cannot at once be discarded compared with the main term. In consequence the J-K model should be regarded as no more and no less than a working model to characterize the molecular rotational aspect of solid methanes. Moreover, it is important to note that we are now able to make up for deficiencies of the J-K model without introducing any new difficulties. Then we consider in §6 another important feature of the results of §2. That is, we look for the crystalline field\(^{6}\) which a methane molecule feels in the solid state.\(^{8)}\) Furthermore, we also calculate the crystalline field of a methane molecule substituted in rare gas matrices. The result will be compared with a preliminary result obtained by Cabana\(^{17}\) et al. by analyzing infrared absorption data. Incidentally the significance of this kind of problem should not be underestimated, because theory and experiment can bear so close a comparison that it enables us to test crucially the validity of the approximation method employed in evaluating the intermolecular forces in the present work. In fact, Nishiyama has already calculated the infrared absorption spectra due to a CH\(_4\) and a CH\(_3\)D molecule in rare gas matrices by making use of the results of the present study and succeeded in showing a satisfactory agreement between prediction and observation, which will be published in a forthcoming paper of the present series.

§2. Formal expression for the interaction between methane molecules

Let us assume that the intermolecular potential between two methane molecules consists of three kinds of interatomic interactions: hydrogen-hydrogen interaction,
\( \Phi_{HH}, \) hydrogen-carbon interaction, \( \Phi_{HO}, \) and carbon-carbon interaction, \( \Phi_{oo}. \) Further, we shall assume that each atom-atom potential is a sum of an electrostatic potential (point charge model) and a Lennard-Jones type potential:\(^\text{(1)}\)

\[
\begin{align*}
\Phi_{HH}(R_{ij}) &= \frac{A_{HH}}{R_{ij}^6} - \frac{B_{HH}}{R_{ij}^{12}} + \frac{e_0^2}{R_{ij}}, \\
\Phi_{HO}(R_k) &= \frac{A_{HO}}{R_k^{12}} - \frac{B_{HO}}{R_k^{18}} - \frac{4e_0^3}{R_k}, \\
\Phi_{oo}(R) &= \frac{A_{oo}}{R^{14}} - \frac{B_{oo}}{R^{18}} + \frac{16e_0^3}{R},
\end{align*}
\]  

(2.1) (2.2) (2.3)

where \( R_{ij} = |\mathbf{R} - \mathbf{r}_i + \mathbf{r}_j|, \) \( R_i = |\mathbf{R} - \mathbf{r}_i|, \) \( R_j = |\mathbf{R} + \mathbf{r}_j|, \) \( k = i \) or \( j, \) \( i \) and \( j = 1, 2, 3 \) and \( 4 \) (Fig. 1), and \( e_0 \) is the effective charge associated with a hydrogen atom and \(-4e_0\) one with a carbon atom. Then the intermolecular potential \( V_{12} \) between two methane molecules 1 and 2 is given by

\[
V_{12} = \sum_{i,j=1}^{4} \Phi_{HH}(R_{ij}) + \sum_{i=1}^{4} \Phi_{HO}(R_i) + \sum_{j=1}^{4} \Phi_{HH}(R_j) + \Phi_{oo}(R).
\]  

(2.4)

The potential (2.4) obviously depends on the molecular orientations, which are described by Euler angles \( \omega_1 \) and \( \omega_2, \) as well as the relative position \( \mathbf{R} \) of two molecules. What we shall do in this section is to transform (2.4) into such an expression that it explicitly shows the dependences on \( \mathbf{R}, \) \( \omega_1 \) and \( \omega_2. \) This is achieved by the use of the two-center expansion formulae derived in the previous paper.\(^\text{(1)}\) That is, we shall appeal to the following expressions of \( R_{ij}^{-n} \) and \( R_k^{-m}:\)

\[
\frac{1}{R_{ij}^n} = \sum_{\ell, \ell', \ell'' \geq 0} (-1)^\ell \left[ \frac{(4\pi)^3}{(2\ell + 1)(2\ell' + 1)(2\ell'' + 1)} \right]^{\frac{3}{2}} C(\ell'\ell'' ; 00) \frac{(2\ell + 1)(2\ell' + 1)}{(n-2)!} \times \frac{(n+p+q-l''-3)!!(n+p+q+l''-2)!!(p-l)!!(p+l+1)!!(q-l'')!!(q+l')!!}{\sqrt{\mathbf{R}}} \{1 + \delta_{\delta, n}(\delta_{\ell, \ell'}+\delta_{\ell''})\delta_{\ell', \ell''}(\delta_{p, p'}+\delta_{q, q'}) - 1\} \\
\times \sum_{m, m'} C(\ell'\ell'' ; mm') Y_{\ell, m, m'}^* (\theta, \phi) Y_{\ell, m, m'} \left( \theta_1, \phi_1 \right) Y_{\ell, m', m'} \left( \theta_2, \phi_2 \right)
\]  

(2.5)

\(^\text{1)}\) When the methane molecules are far apart and the separation is large compared to the dimensions of the molecules, it is well known that the dispersion force does not have anisotropic part because the polarizability tensor is spherical. However, it is not true in the solid state, where the molecules are close to each other and thus the lowest-order perturbation theoretical treatment does not give a correct result.
and

\[
\frac{1}{R_k''} = \frac{1}{R_k'} \frac{4\pi}{(n'-2)!} \sum_{l=0}^{\infty} (-1)^{(k)} \frac{(n'+p-l-3)!!(n'+p+l-2)!!}{(p-l)!!(p+l+1)!!} \left( \frac{r}{R} \right)^p \\
\times (1 + \delta_{l,m}(\theta_p, \varphi_{l-1}) \sum_{m} Y_{l,m}^*(\theta, \varphi) Y_{l,m}(\theta, \varphi),
\]

where \( R = (R, \theta, \varphi), \ r_k = (r, \theta_k, \varphi_k) \), \( r \) is the CH-bond length, \( n \) and \( n' \) are positive integers, \((-2)!! = (1)!! = 1, \ p = l, l+2, l+4, \cdots \), and \( q = l', l'+2, l'+4, \cdots, C(l'l''; mm') \) are the Clebsch-Gordan coefficients and \( Y_{l,m}(\theta, \varphi) \) the spherical harmonics.

Application of (2.5) and (2.6) to (2.4) is straightforward. First we have to carry out the summation \( \sum_{k=1}^{4} Y_{l,m}(\theta_k, \varphi_k) \). For this purpose we define a standard orientation of the methane molecule under question as shown in Fig. 2. Now suppose the molecule is rotated through Euler angles \( \omega \) from the standard position, so that the \( k \)-th proton moves from \( (\theta_k^0, \varphi_k^0) \) to \( (\theta_k, \varphi_k) \). Corresponding to this rotation, spherical harmonics are transformed as

\[
Y_{l,m}(\theta_k, \varphi_k) = \sum_{m} \Xi_{l,m}(\omega) Y_{l,m}(\theta_k^0, \varphi_k^0).
\]

Here \( \Xi_{l,m}(\omega) \) denote Wigner's rotational functions. From (2.7), we obtain

\[
\sum_{k=1}^{4} Y_{l,m}(\theta_k, \varphi_k) = \alpha_l T_{l,m}(\omega),
\]

where

\[
T_{l,m}(\omega) = \sum_{m} A_{l,m} \Xi_{l,m}(\omega),
\]

\[
A_{l,m} = \alpha^{-1}_l \{ (-)^m + 1 \} \{ (-)^{l'-m} + 1 \} Y_{l,m}(\beta, \pi/4),
\]

where \( \beta \) is the constant defined by \( \cos \beta = 1/\sqrt{3} \) and \( \alpha_l \) is chosen so that each \( T_{l,m}(\omega) \) is normalized to \( 8\pi \). The numerical values of the non-vanishing elements of \( A_{l,m} \) and of \( \alpha_l/4 \) of lower orders are given in Table I. From this table, we observe that the \( \omega \)-dependence of (2.8) has the \( T_a \)-symmetry, as it should be expected.

The interaction potential (2.4) between two methane molecules can now be rearranged in such a way that it consists of an isotropic part, a part dependent on \( \omega_i \), only, a part dependent on \( \omega_2 \) only and a part that depends on both \( \omega_1 \) and
Table 1. Numerical values of the non-vanishing elements of $A_{i,M}$ and $a_{i/4}$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$A_{i,M}$</th>
<th>$a_{i/4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$A_{0,0} = 1$</td>
<td>$\frac{1}{\sqrt{4\pi}}$</td>
</tr>
<tr>
<td>3</td>
<td>$A_{3,2} = -A_{3,-2} = \frac{i\sqrt{14}}{2}$</td>
<td>$\frac{\sqrt{5}}{3\sqrt{4\pi}}$</td>
</tr>
<tr>
<td>4</td>
<td>$A_{4,0} = -\frac{\sqrt{21}}{2}$, $A_{4,4} = -\frac{\sqrt{30}}{4}$</td>
<td>$\frac{\sqrt{21}}{9\sqrt{4\pi}}$</td>
</tr>
<tr>
<td>6</td>
<td>$A_{6,0} = \frac{\sqrt{661}}{8}$, $A_{6,4} = -\frac{\sqrt{91}}{4}$</td>
<td>$\frac{4\sqrt{2}}{9\sqrt{4\pi}}$</td>
</tr>
<tr>
<td>7</td>
<td>$A_{7,3} = -A_{7,-3} = -i\frac{\sqrt{65}}{4}$, $A_{7,5} = -A_{7,-5} = -i\frac{\sqrt{55}}{4}$</td>
<td>$\frac{\sqrt{273}}{27\sqrt{4\pi}}$</td>
</tr>
<tr>
<td>8</td>
<td>$A_{8,0} = \frac{\sqrt{561}}{8}$, $A_{8,4} = \frac{\sqrt{714}}{24}$, $A_{8,8} = \frac{\sqrt{6630}}{48}$</td>
<td>$\frac{\sqrt{33}}{27\sqrt{4\pi}}$</td>
</tr>
</tbody>
</table>

That is, using (2.5) $\sim$ (2.9) one arrives at the following result:

$$V_{12} = U(R) + V(R, \theta, \varphi; \omega_1) + V(R, \pi - \theta, \varphi + \pi; \omega_2) + W(R, \theta, \varphi; \omega_1, \omega_2),$$

$$V(R, \theta, \varphi; \omega) = \sum_{l \geq 0} C(V(R; l) \sum_{m} Y_{l,m}^{*}(\theta, \varphi) T_{l,m}(\omega),$$

$$W(R, \theta, \varphi; \omega_1, \omega_2) = \sum_{l \geq 0} \sum_{m, m'} C(Ull'; \omega) Y_{l,m}^{*}(\theta, \varphi) T_{l,m}(\omega_1) T_{l,m'}(\omega_2).$$

Here the angular-independent quantities $U(R)$, $C(V(R; l)$ and $C(Ull'; \omega)$ are defined as follows:

$$U(R) = 4^{2} \sum_{p,q} \left\{ \frac{A_{HH}(n + p + q - 2)!}{(n - 2)! R^{n}} - \frac{B_{HH}(p + q + 4)!}{4! R^{n}} \right\} \frac{1}{(p + 1)! (q + 1)!} \left( \frac{r}{R} \right)^{p+q},$$

$$+ 8 \sum_{p} \left\{ \frac{A_{HH}(n' + p - 2)!}{(n' - 2)! R^{n'}} - \frac{B_{HH}(p + 4)!}{4! R^{n'}} \right\} \frac{1}{(p + 1)!} \left( \frac{R}{r} \right)^{p} + \frac{A_{00}}{R^{n'}} - \frac{B_{00}}{R^{n'}},$$

(2.13)
where \( p, q = 0, 2, 4, \ldots \),

\[
\mathcal{U}(R; I) = 4\pi\alpha^4 \left[ \frac{A_{HH}(R, n, l)}{(n-2)!R^n} - \frac{B_{HH}(R, 6, l)}{4!R^6} \right] + \left[ \frac{A_{H2}(R, n', l)}{(n'-2)!R^{n'}} - \frac{B_{H2}(R, 6, l)}{4!R^6} \right],
\]

and

\[
\mathcal{W}(R; l' l'') = (-\gamma') \left[ \frac{(4\pi)^9 (2l + 1) (2l' + 1)}{2l'' + 1} \right]^{1/2} C(l' l'' ; 00) \alpha_\gamma \alpha_{\nu'}
\times \left[ \frac{A_{HH}(R, n, l, l', l'')}{(n-2)!R^n} - \frac{B_{HH}(R, 6, l, l', l'')}{4!R^6} \right] + (-\gamma')
\times \left[ \frac{(4\pi)^9}{(2l + 1) (2l' + 1) (2l'' + 1)} \right]^{1/2} \left[ \frac{(2l'')!}{(2l)! (2l')!} \right]^{1/2} \alpha_\nu \alpha_{\nu'} \varepsilon_{\nu \\nu'}^{l''} \delta_{l' \nu, \nu'}.
\]

We have introduced the following notations:

\[
X(R, n, l) = \sum_{p,q} \frac{(n + p + q - l - 3)!! (n + p + q + l - 2)!!}{(p-l)!!(p+l+1)!!(q+1)!!} \left( \frac{r}{R} \right)^{p+q},
\]

\[
Z(R, n, l) = \sum_{p} \frac{(n + p - l - 3)!! (n + p + l - 2)!!}{(p-l)!!(p+l+1)!!} \left( \frac{r}{R} \right)^{p},
\]

and

\[
X(R, n, l, l', l'') = \sum_{p, q, r} \frac{(n + p + q' - l'' - 3)!! (n + p + q' + l'' - 2)!!}{(p-l)!!(p+l+1)!!(q'-l')!!(q'+l'+1)!!} \left( \frac{r}{R} \right)^{p+q'},
\]

where \( p = l, l+2, l+4, \ldots \), \( q = 0, 2, 4, \ldots \), and \( q' = l', l' + 2, l' + 4, \ldots \).

A few observations may be made before closing this section. In (2.11) and (2.12) the summations over \( l \) and \( l' \) start from \( l, l' = 3 \). This corresponds to the fact that the methane molecule has \( T_a \)-symmetry. Next, as is well known, the electrostatic interactions are included only in \( W(R, \theta, \varphi; \omega_1, \omega_2) \) in the form of multipole-multipole interactions, the lowest of which is an octopole-octopole interaction. Stevens has developed group-theoretical arguments and found a result which corresponds to the terms up to \( l, l' = 4, l'' = 0 \) in (2.11) and (2.12). However, he has taken into account only the first summations on the right-hand side of (2.4), completely neglecting the contributions from \( \theta_{\omega_2} \) and \( \omega_{\theta_0} \) and those from the electrostatic interactions. We should like to note here that these interactions make significant contributions to the anisotropic as well as isotropic parts, as will be shown below.
§ 3. **Numerical values of the parameters characterizing the interatomic potentials**

In order to put forward quantitative discussions, we now have to estimate the numerical values of various parameters involved in the assumed interatomic interactions, \((2\cdot1) \sim (2\cdot3)\). For this purpose we may have recourse to elaborate and thorough investigations done by Bartell,\(^9\) Hendrickson,\(^9\) Kitaigorodskii and his co-workers\(^{10},^{11}\) and others. Unfortunately the repulsive part of the interatomic potential is very often expressed in a simple exponential form, whereas we have chosen instead an inverse power law in order to avoid technical difficulties in applying the two-center expansion formulae to the present problem. It is, therefore, necessary to transform the former into the latter by choosing appropriate values of \(A_{HH}\) and \(n\) and \(A_{HC}\) and \(n'\).\(^*\) Needless to say this transformation cannot be done in a unique way. We have done this so that the new potential coincides with the original one at the point of its minimum and at the point 0.5Å inward therefrom. The reason for this is that the main contribution from the repulsive part comes from that region in the solid state.\(^**\) Thus we have obtained three sets of interatomic potentials \(a\), \(b\) and \(c\) which are due to Bartell, Kitaigorodskii and Hendrickson, respectively. The results are summarized in Table II. We shall make a comparative study of these potentials in the following sections and in subsequent papers.

As regards the value of \(\varepsilon_0\), there are again somewhat divergent data in the

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
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<tbody>
<tr>
<td>(n)</td>
<td>10</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>(A_{HH})</td>
<td>(9.42 \times 10^5)</td>
<td>(12.57 \times 10^5)</td>
<td>(4.86 \times 10^5)</td>
</tr>
<tr>
<td>(B_{HH})</td>
<td>(2.48 \times 10^4)</td>
<td>(2.17 \times 10^4)</td>
<td>(2.48 \times 10^4)</td>
</tr>
<tr>
<td>(n')</td>
<td>12</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>(A_{HC})</td>
<td>(3.53 \times 10^7)</td>
<td>(3.28 \times 10^7)</td>
<td>(1.88 \times 10^6)</td>
</tr>
<tr>
<td>(B_{HC})</td>
<td>(6.29 \times 10^4)</td>
<td>(6.88 \times 10^4)</td>
<td>(6.29 \times 10^4)</td>
</tr>
<tr>
<td>(n'')</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_{CC})</td>
<td>(1.51 \times 10^8)</td>
<td>(1.52 \times 10^8)</td>
<td>(8.36 \times 10^8)</td>
</tr>
<tr>
<td>(B_{CC})</td>
<td>(1.64 \times 10^8)</td>
<td>(2.12 \times 10^8)</td>
<td>(1.64 \times 10^8)</td>
</tr>
</tbody>
</table>

\(a\): Bartell\(^9\) \hspace{1cm} \(b\): Kitaigorodskii\(^{10},^{11}\) \hspace{1cm} \(c\): Hendrickson\(^9\)

\(^*\) To \(\theta_{ee}\) we can apply the exponential form directly.

\(^**\) Furthermore, the slope of the potential, which is significant in the present calculations, is well reproduced in this region.
range $0.1e$ to $0.2e$, $e$ being the electronic charge. Pitzer\textsuperscript{15} gives $e_0=0.078e$ from a quantum mechanical calculation. Kimel et al.\textsuperscript{19} estimate it at $0.1e$ by analyzing intensities of the infrared absorption bands. Recently Ozier and Fox\textsuperscript{20} have succeeded in determining the octopole moment of methane molecule from the collision-induced rotational spectra, which yields $e_0=0.22e$. In the following discussion we shall take up two values, $0.1e$ and $0.2e$, for the sake of completeness.

§ 4. The isotropic intermolecular potential

We have calculated from (2·13) the isotropic part of the intermolecular potential, putting the length of the CH bond equal to 1.09Å. The results are plotted in Fig. 3. For comparison, a currently accepted “12–6” potential\textsuperscript{22} is also shown by the thin solid line in the same figure. We clearly observe large discrepancies in the repulsive part. It should be remembered now that the 12–6 potential, cited above, was obtained through analyzing the second virial coefficient data obtained in the high temperature region ($>200K$) and that the anisotropic parts of the potential was not taken into account. As to the first point, Byrne Jones and Staveley\textsuperscript{22} have shown that a “18–6” potential is superior to the “12–6” form in accounting for the virial coefficient in the low temperature region (100–230K). Their result is also shown by the dashed curve in Fig. 3. It is interesting to note that it goes between the curves a and b in the deepest region of the potential which is most important in discussing various phenomena in the condensed phases. We are thus tempted to regard a as the best of three so far as the isotropic part is concerned.
§ 5. The anisotropic interaction which depends on the orientations of both molecules

The purpose of the present section is to evaluate from (2·12) the anisotropic parts of the intermolecular potential in the solid state. We shall devote ourselves to looking for the main terms of the expansion in order to truncate and reshape it in a compact form. By doing so we will be able to examine the limitation of the validity of the James-Keenan model, according to which the orientation-dependent interaction in solid methane is described by an effective octopole-octopole interaction, as was already mentioned in Introduction.

We have estimated the numerical values of \( \mathcal{W}(R; II'') \) from (2·15), putting \( R = 4.115 \text{Å} \) for the distance between nearest-neighboring molecules in the solid state. The results are shown in Table III. \( \mathcal{W}(R; 336) \) and \( \mathcal{W}(R; 448) \) are given two figures, the upper ones corresponding to \( \epsilon_0 = 0.1e \) and the lower ones to \( \epsilon_0 = 0.2e \). The values of \( \mathcal{W}(R; 347) \), etc., are not shown in the table, because they have a tendency to cancel each other in (2·12) because of the relations \( \mathcal{W}(R; 347) = -\mathcal{W}(R; 437) \).)\(^a\) As is obvious from the table, \( \mathcal{W}(R; 336) \) has the largest absolute values in all cases. This immediately means that the main terms of the anisotropic interaction can be identified with an effective octopole-octopole interaction which is nothing but the spirit of James and Keenan. However, there appear other terms which cannot immediately be neglected. Now,

\[
\begin{array}{c|c|c|c}
\mathcal{W}(R; 336) & a & b & c \\
-39.9 & -24.2 & -14.1 \\
-55.8 & -40.2 & -31.0 \\
\mathcal{W}(R; 334) & 19.3 & 14.1 & 6.89 \\
\mathcal{W}(R; 332) & -16.8 & -11.5 & -6.50 \\
\mathcal{W}(R; 330) & 28.3 & 18.9 & 11.2 \\
\mathcal{W}(R; 448) & 8.55 & 5.56 & 3.30 \\
9.05 & 6.06 & 3.80 \\
\mathcal{W}(R; 446) & -3.59 & -2.61 & -1.50 \\
\mathcal{W}(R; 444) & 2.38 & 1.77 & 1.05 \\
\mathcal{W}(R; 442) & -1.95 & -1.73 & -0.98 \\
\mathcal{W}(R; 440) & 3.76 & 2.92 & 1.72 \\
\end{array}
\]

The columns \( a, b \) and \( c \) have the same meaning as in Table II.

\(^a\) The numerical value of, say, \( \mathcal{W}(R; 347) \) is equal at most to 22.2(K).
as the first approximation we may discard terms with \( \mathcal{W}(R; 44l^{\prime\prime}) \) and higher order terms in (2·12), keeping only those terms with \( \mathcal{W}(R; 33l^{\prime\prime}) \) with \( l^{\prime\prime} = 6, 4, 2 \) and 0. Then, as is easily seen, it turns out that the required anisotropic interaction still has exactly the same dependence on \( \omega_1 \) and \( \omega_2 \) as the octopole-octopole interaction, although the dependences on the relative position of the two interacting molecules are no longer the same. Again as seen from Table III, the contributions from \( \mathcal{W}(R; 334) \) and \( \mathcal{W}(R; 332) \) have a tendency to cancel each other. Thus the main defect of the James-Keenan model comes from \( \mathcal{W}(R; 330) \), which can, however, be easily included into the J-K model if only one assigns an appropriate value to \( C(336; 00) \) in (2·12). Consequently we would like to say that the J-K model, if it is modified as mentioned above, is really qualified as a working model which enables one to abstract the essential features of the rotational motion in solid methane. We are now examining the properties of the modified J-K model as applied to the solid methane. The results will be reported in a forthcoming paper.

§ 6. Crystalline field

Now let us turn to the anisotropic interaction (2·11), which depends only on the orientation of a member of the pair of molecules. Let us suppose a methane molecule in the solid state. It is surrounded by twelve neighbors that affect the rotational motion of the central molecule via (2·11). Since each of these interaction potentials is a function of the orientation of the central molecule, they may be regarded to make up a kind of crystalline field for the central molecule. An analogous situation is realized when a methane molecule is substituted in a rare gas matrix.

King and Hornig\(^{23}\) have provided a theoretical framework to describe the crystalline field based on group-theoretical arguments. On the other hand, vibration-rotational spectra of methane molecule have been observed in rare gas matrices\(^{17,24,26}\) as well as in solid methane.\(^{26,27}\) Cabana et al.\(^{17}\) have indeed made a preliminary analysis of their infrared absorption spectra with the intention of determining the crystalline field, based on King and Hornig's work. Since the crystalline field is expected to play an important role in understanding the molecular rotation in solid methane,\(^9\) we want to find its explicit expression.

In the first subsection we shall treat a methane molecule in solid methane, and then in the next subsection we shall proceed to the problem in rare gas matrices.

**Crystalline field in solid methane**

A molecule in solid methane has 12 nearest-neighboring molecules around it (Fig. 4). Let us denote the orientation of the central molecule by \( \omega \). Then, the crystalline field \( V(\omega) \) which the molecule feels in the crystal is obtained by summing...
up the contributions, given by (2.11), from each of its 12 nearest-neighbors. Thus one has

\[ V(\omega) = \sum_{l \leq 3} C_{l}^{(R)}(R; l) \sum_{m} q_{l,m} T_{l,m}(\omega), \quad (6.1) \]

\[ q_{l,m} = \sum_{r=1}^{12} Y_{l,m}^{*}(\theta, \varphi). \quad (6.2) \]

The coefficient \( C_{l}^{(R)}(R; l) \) is defined by (2.14). The summation in (6.2) can straightforwardly be carried out with the result:

\[ q_{l,m} = (-)^{(m+|m|)/2} (1 + (-)^{m}) (1 + i^{m}) \times \left[ \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \{1 + (-)^{m+1}\} \times P_{l}^{(m)}(1/\sqrt{2}) + P_{l}^{(m)}(0) e^{-i\pi m/4}, \quad (6.3) \]

where \( P_{l}^{(m)} \) denotes the associated Legendre function. The numerical values of the nonvanishing elements of \( q_{l,m} \) are given in Table IV. From this and Table I, we find that the crystalline field \( V(\omega) \) has the symmetry \( T_d \times O_h \).

It is convenient to introduce the following notation:

\[ V_{l}(\omega) = A_{l} \sum_{m} q_{l,m} T_{l,m}(\omega), \quad (6.4) \]

where \( A_{l} \) is the normalization constant such that

\[ \int |V_{l}(\omega)|^{2} d\omega = 8\pi^{3}. \]

Thus one arrives at the final form of the crystalline field:

Table IV. Numerical values of the non-vanishing coefficients of \( q_{l,m} \).

<table>
<thead>
<tr>
<th>( q_{l,m} )</th>
<th>( q_{l,0} )</th>
<th>( q_{l,\pm 2} )</th>
<th>( q_{l,\pm 4} )</th>
<th>( q_{l,\pm 6} )</th>
<th>( q_{l,\pm 8} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_{l,0} )</td>
<td>[ -\frac{21}{4\sqrt{4\pi}} ]</td>
<td>[ -3\sqrt{70}/8\sqrt{4\pi} ]</td>
<td>[ -3\sqrt{13}/16\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 13}/32\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 11.17}/2^{6}\sqrt{4\pi} ]</td>
</tr>
<tr>
<td>( q_{l,\pm 2} )</td>
<td>[ -\frac{21}{4\sqrt{4\pi}} ]</td>
<td>[ -3\sqrt{70}/8\sqrt{4\pi} ]</td>
<td>[ -3\sqrt{13}/16\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 13}/32\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 11.17}/2^{6}\sqrt{4\pi} ]</td>
</tr>
<tr>
<td>( q_{l,\pm 4} )</td>
<td>[ -\frac{21}{4\sqrt{4\pi}} ]</td>
<td>[ -3\sqrt{70}/8\sqrt{4\pi} ]</td>
<td>[ -3\sqrt{13}/16\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 13}/32\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 11.17}/2^{6}\sqrt{4\pi} ]</td>
</tr>
<tr>
<td>( q_{l,\pm 6} )</td>
<td>[ -\frac{21}{4\sqrt{4\pi}} ]</td>
<td>[ -3\sqrt{70}/8\sqrt{4\pi} ]</td>
<td>[ -3\sqrt{13}/16\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 13}/32\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 11.17}/2^{6}\sqrt{4\pi} ]</td>
</tr>
<tr>
<td>( q_{l,\pm 8} )</td>
<td>[ -\frac{21}{4\sqrt{4\pi}} ]</td>
<td>[ -3\sqrt{70}/8\sqrt{4\pi} ]</td>
<td>[ -3\sqrt{13}/16\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 13}/32\sqrt{4\pi} ]</td>
<td>[ 3\sqrt{2.7 \times 11.17}/2^{6}\sqrt{4\pi} ]</td>
</tr>
</tbody>
</table>
H. Yasuda

\[ V(\omega) = \sum_{l=4} B_{\beta_l} V_l(\omega), \quad (6.5) \]

where \( \beta_l \) are dimensionless constants defined by

\[ B_{\beta_l} = A_l^{-1} C R(R; l), \quad (6.6) \]

\( B \) being a rotational constant of methane molecule (= 7.558K).

For practical applications it suffices to include terms up to \( l = 6 \) in (6.6), since the remaining terms make negligibly small contributions. The first two \( V_l \)'s may be written down here:

\[ V_4(\omega) = \sqrt{9} \left[ \frac{7}{12} \mathfrak{D}_{k}^{(4)}(\omega) + \frac{\sqrt{70}}{24} \{ \mathfrak{D}_{k}^{(4)}(\omega) + \mathfrak{D}_{k-4}^{(4)}(\omega) + \mathfrak{D}_{k+4}^{(4)}(\omega) \} \right. \]

\[ + \frac{5}{24} \{ \mathfrak{D}_{k-4}^{(4)}(\omega) + \mathfrak{D}_{k+4}^{(4)}(\omega) + \mathfrak{D}_{k+4}^{(4)}(\omega) \} \left. \right], \quad (6.7) \]

\[ V_6(\omega) = \sqrt{13} \left[ \frac{1}{8} \mathfrak{D}_{k}^{(6)}(\omega) - \frac{\sqrt{14}}{16} \{ \mathfrak{D}_{k}^{(6)}(\omega) + \mathfrak{D}_{k-4}^{(6)}(\omega) + \mathfrak{D}_{k+4}^{(6)}(\omega) \} \right. \]

\[ + \frac{7}{16} \{ \mathfrak{D}_{k-4}^{(6)}(\omega) + \mathfrak{D}_{k+4}^{(6)}(\omega) + \mathfrak{D}_{k+4}^{(6)}(\omega) \} \left. \right], \quad (6.8) \]

The numerical values of \( \beta_4 \) and \( \beta_6 \) are given in Table V. The behavior of the crystalline fields obtained is demonstrated in Fig. 5 for the special case \( \omega = \{x, 0, 0\} \). One first observes that the orientation \( \{0, 0, 0\} \) is most stable, as it should be expected. Next the three crystalline fields \( a, b \) and \( c \) differ considerably from each other. We wish, therefore, to know which is the best. It is for this purpose that we treat analogous problems in rare gas matrices in the next sub-

![Fig. 5. Demonstration of the crystalline field (6.5) in the solid state. Curves a, b and c have the same meaning as in Fig. 3; \( \omega = \{x, 0, 0\} \).](https://academic.oup.com/ptp/article-abstract/45/5/1361/1912776)

| Table V. Predicted values of \( \beta_4 \) and \( \beta_6 \) which characterize the crystalline field in solid CH₄. |
|-----------------|-----------------|-----------------|-----------------|
|                 | \( a \)          | \( b \)          | \( c \)          |
| \( \beta_4 \)   | 6.10             | 3.17             | 0.76             |
| \( \beta_6 \)   | -8.05            | -5.57            | -2.66            |

The meanings of \( a, b \) and \( c \) are the same as in Table II.
section, because predictions on these problems can crucially be tested by comparing with experiment.

**Crystalline fields of a methane molecule in rare gas matrices**

Now we discuss crystalline fields which a methane molecule experiences in rare gas matrices. Let us suppose a methane molecule is substituted for a rare gas molecule in an FCC rare gas crystal.

First of all, we have to know the interaction potential between a hydrogen atom and a rare gas molecule \( X \), in the form of the Lennard-Jones type potential. To be more specific, we may assume that

\[
\Phi_{HX}(R) = \frac{A_{HX}}{R^{12}} - \frac{B_{HX}}{R^6}.
\]

In order to determine the values of the parameters \( A_{HX} \) and \( B_{HX} \), we appeal to the so-called combination rule. Assume that both \( \Phi_{XX} \) and \( \Phi_{HH} \) are known in the form

\[
\Phi(R) = \frac{n}{n-6} \left( \frac{6}{n} \right)^{\frac{1}{2}} \varepsilon \left\{ \left( \frac{\sigma}{R} \right)^{n} - \left( \frac{\sigma}{R} \right)^{6} \right\},
\]

then \( \Phi_{HX} \) can also be expressed in the same form with

\[
\varepsilon_{HX} = (\varepsilon_{HH} \cdot \varepsilon_{XX})^{\frac{1}{2}}, \quad \sigma_{HX} = (\sigma_{HH} + \sigma_{XX})/2.
\]

According to this rule, one readily obtains

\[
A_{HX} = 4 \varepsilon_{HX} \sigma_{HX}^2, \quad B_{HX} = 4 \varepsilon_{HX} \sigma_{HX}.
\]

The values of these parameters are listed in Table VI.\(^3\)

Following exactly the same procedure as in the last subsection, we can arrive at the crystalline field in the form (6·5) with

| Table VI. Numerical values of the parameters \( \varepsilon_{HX}(K) \) and \( \sigma_{HX}(\text{Å}) \) which characterize the interatomic interaction between hydrogen atom and rare gas atom. |
|---|---|---|---|---|---|
|  | \( a \) |  | \( b \) |  | \( c \) |
| \( \varepsilon_{HX} \) | \( \sigma_{HX} \) | \( \varepsilon_{HX} \) | \( \sigma_{HX} \) | \( \varepsilon_{HX} \) | \( \sigma_{HX} \) |
| Ar | 48.6 | 2.96 | 65.8 | 2.86 | 79.8 | 2.77 |
| Kr | 58.0 | 3.06 | 78.6 | 2.96 | 95.4 | 2.87 |
| Xe | 66.0 | 3.31 | 89.3 | 3.21 | 108.4 | 3.12 |

The letters \( a, b \) and \( c \) have the same meaning as in Table II.

\(^3\) The data of rare gas molecules were taken from Ref. 21).
Table VII. Predicted values of $\beta_4$ and $\beta_6$ which characterize the crystalline fields in rare gas matrices.

<table>
<thead>
<tr>
<th></th>
<th>$R_X^{\text{Ar}}$ (Å)</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta_4$</td>
<td>$\beta_6$</td>
<td>$\beta_4$</td>
<td>$\beta_6$</td>
<td>$\beta_4$</td>
</tr>
<tr>
<td>Ar</td>
<td>3.755</td>
<td>13.2</td>
<td>-16.1</td>
<td>10.8</td>
<td>-13.9</td>
</tr>
<tr>
<td>Kr</td>
<td>3.992</td>
<td>7.16</td>
<td>-8.29</td>
<td>5.72</td>
<td>-7.17</td>
</tr>
<tr>
<td>Xe</td>
<td>4.335</td>
<td>4.64</td>
<td>-4.81</td>
<td>3.79</td>
<td>-4.27</td>
</tr>
</tbody>
</table>

$R_X$: the distance between nearest-neighboring molecules in rare gas crystal.

Columns $a$, $b$ and $c$ have the same meaning as in Table II.

Column $d$ gives the crystalline field obtained by Cabana et al.\textsuperscript{17}

\begin{equation}
B\beta_i = 4\pi\alpha_i A_i^{-1} \left\{ \frac{A_{HHZ}(R_X, 12, I)}{10!R_X^{12}} - \frac{B_{HHZ}(R_X, 6, I)}{4!R_X^6} \right\}.
\end{equation}

Here $R_X$ denotes the distance between the nearest-neighboring pair of molecules in the rare gas matrix under discussion. The results of the numerical calculations are shown in Table VII and in Fig. 6. Column $d$ of this table gives the result of Cabana et al.\textsuperscript{17} for the sake of comparison.

Fig. 6. The crystalline field of a methane molecule in Xe matrix for the special case $\omega = [\alpha, 0, 0]$. The curves $a$, $b$ and $c$ have the same meaning as in Fig. 3. The dash-dotted curve shows the crystalline field given by Cabana et al.\textsuperscript{17}

§ 7. Summary

We have discussed the interaction between methane molecules in solid state under the assumption of the pairwise interatomic interaction. The calculations have been made on the basis of the general theory of two-center expansion developed by Yamamoto and the present author and of the empirical interatomic potentials given by Bartell,\textsuperscript{9} Kitaigorodskii\textsuperscript{10,11} and Hendrickson\textsuperscript{9} (Table II).

A formal expression for the intermolecular interaction has been derived in such a form reflecting both molecular orientations and molecular symmetry as (2·10) in § 2. The isotropic part of this expression has been compared with the potentials obtained from the second virial coefficients in § 4. The anisotropic
parts (2·12) dependent on the orientation of both molecules have been worked out in § 5. The validity and the necessary modification of the James-Keenan model have been discussed on the basis of the results obtained. Finally in § 6, the crystalline fields have been calculated, by making use of (2·11), which a methane molecule feels in rare gas matrices as well as in solid methane. The results are given by (6·5) together with Tables V and VII.

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References

14) The correction will be published.
15) N. Uryu and R. Hirota, Memoirs of the Faculty of Science, Kyushu University, Ser. B 2 (1956), 64.