Normal Vibration and Internal Rotation of Ethane-type Molecules

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Internal rotation is the motion in which one part of a molecule moves relatively to the other parts of the molecule.[1] In some molecules the parts are so tightly bound that their relative motion can be treated as one of the vibrational modes, but in other molecules the groups are connected loosely with each other and are able to rotate almost freely. According to the general discussion given by Born and Oppenheimer[2], the molecular vibration can approximately be treated separately from the rotation, but internal rotation does not allow such a simplified treatment; one must apply a method suitable for each case.

Many researches have been carried out on the coupling of internal rotation with overall rotation. Even in the cases where the energy of internal rotation is small or comparable in magnitude with that of overall rotation, studies have been restricted to particular types of molecules, such as symmetric[3,4] or almost symmetric top[5,6], and main interest has been concerned with the complicated rotational spectra observed by the microwave spectroscopy[7].

The other coupling scheme, the interaction of internal rotation with vibrations, is important when the energy of internal rotation becomes comparable with that of vibrations. Usually internal rotation is ignored in analyzing the normal modes, but the vibrations of low frequencies, such as deformation vibrations, do couple strongly with the internal rotation, and hence the force constants obtained by the usual procedure may sometimes be in considerable error.

At present, data are often insufficient in number to determine the general quadratic force field, and hence it is necessary to assume a particular force field, for instance, valence force field[8]. The most satisfactory field seems to be of the Urey-Bradley type[9]; the characteristic of this force field is the explicit introduction of the repulsive forces between two nonbonded atoms. Usually, however, one takes into consideration only the next nearest interaction, that is, the interaction between the next nearest atom pairs, and in this approximation the internal rotation and accordingly its coupling with the vibration are completely ignored in the analysis of the normal modes. In order to discuss the internal rotation the procedure must be extended to include the atom pairs, whose interaction hinders the internal rotation. In this paper the discussion will be restricted for simplicity to a particular case: the ethane-type molecules and as one of the most typical examples hexachloroethane will be treated in detail.

The analysis of the normal vibrations gives a basis of calculating mean square amplitudes of atom pairs (abbreviated as mean amplitudes) obtained by the recent electron diffraction experiment[10]. The mean amplitudes of some atom pairs relate closely with the internal rotation, and when one compares such observed amplitudes with those calculated on the basis of the normal coordinate analysis, an estimate can be made on the value of the potential barrier restricting the internal

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1) S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, Inc., New York, 1954.

2) M. Born and J. R. Oppenheimer, *Ann. Physik*, **84**, 457 (1927).

3) H. H. Nielsen, *Phys. Rev.* **40**, 445 (1832).

4) D. Kivelson, *J. Chem. Phys.* **22**, 1733 (1954); **23**, 2230, 2236 (1955).

5) J. S. Koehler and D. M. Dennison, *Phys. Rev.* **57**, 1006 (1940).

6) D. G. Burkhard and D. M. Dennison, ibid. **84**, 408 (1951); E. V. Ivash and D. M. Dennison, *J. Chem. Phys.* **21**, 1804 (1953); E. Bright Wilson, Jr., C. C. Lin and D. R. Lide, ibid. **23**, 136 (1955); K. T. Hecht and D. M. Dennison, ibid. **26**, 31, 48 (1957);, R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., ibid. **26**, 1695 (1957).

7) See W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy", John Wiley & Sons, Inc., New York, 1953. pp 105-106; C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw Hill Book Co., Inc., New York, 1955.

8) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol II, D. Van Nostrand Co., Inc., New York, 1944.

9) T. Shimanouchi, *J. Chem. Phys.* **17**, 245, 734, 848 (1949).

10) Y. Morino, K. Kuchitsu, and T. Shimanouchi, ibid. **20**, 726 (1952); Y. Morino, K. Kuchitsu, A. Takahashi, and K. Maeda, ibid. **21**, 1927 (1957); Y. Morino and E. Hirota, ibid. **23**, 737 (1955).

rotation[11]. This method of the determination of the potential barrier is very interesting and important since there are at present no other possible ways of obtaining the barrier height of ethane-type molecules, except the thermodynamic methods.

Analysis of the Normal Modes

The potential energy usually used in the analysis of the normal modes consists of terms which are functions of three kinds of coordinate: the bond lengths, the bond angles, and the distances between the next nearest atoms[12]. As stated previously, in this expression for the potential energy there are no forces restricting the rotation about the central bond ($X-X'$ axis in Fig. 1). Two types of coordinates, the distances such as Y_1-Y_2' and the angles projected along the $X-X'$ axis such as $\phi_{12}=\angle Y_1XY_2'$, may be used to express the interaction between twe XY_3 groups, though the distances such as $Y_1Y'_1$ are so long that the interactions associated with them can be ignored. Four new force constants being added to these coordinates, the Urey-Bradley type expression for potential energy becomes

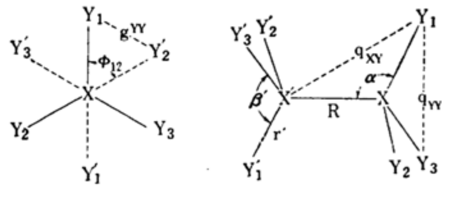

Fig. 1. Schematic diagram of X_2Y_6-type molecule

$$\begin{aligned}2V=&2{K'}_{XX}R\varDelta R+K_{XX}(\varDelta R)^2\\&+2{K'}_{XY}r[\sum(\varDelta r_i)+\sum(\varDelta r'_i)]\\&\quad+K_{XY}[\sum(\varDelta r_i)^2+\sum(\varDelta r'_i)^2]\\&+2{H'}_{XXY}r^2[\sum(\varDelta\alpha_i)+\sum(\varDelta\alpha'_i)]\\&\quad+H_{XXY}r^2[\sum(\varDelta\alpha_i)^2+\sum(\varDelta\alpha'_i)^2]\\&+2{H'}_{YXY}r^2[\sum(\varDelta\beta_{ij})+\sum(\varDelta\beta'_{ij})]\\&\quad+H_{YXY}r^2[\sum(\varDelta\beta_{ij})^2+\sum(\varDelta\beta'_{ij})^2]\\&+2{F'}_{XY}q_{XY}[\sum(\varDelta q_i)+\sum(\varDelta q'_i)]\\&\quad+F_{XY}[\sum(\varDelta q_i)^2+\sum(\varDelta q'_i)^2]\\&+2{F'}_{YY}q_{YY}[\sum(\varDelta q_{ij})+\sum(\varDelta q'_{ij})]\\&\quad+F_{YY}[\sum(\varDelta q_{ij})^2+\sum(\varDelta q'_{ij})^2]\\&+2{J'}_{YY}g^{YY}\sum(\varDelta {g^{YY}}_{ij})\\&\quad+J_{YY}\sum(\varDelta {g^{YY}}_{ij})^2\\&+2\Phi' r^2\sum(\varDelta\phi_{ij})+\Phi r^2\sum(\varDelta\phi_{ij})^2\end{aligned}\tag{1}$$

where the last four terms are newly introduced. R denotes the equilibrium distance of $X-X'$, r that of $X-Y$ or of $X'-Y'$, q_{XY} that of $X'-Y$ or of $X-Y'$, q_{YY} that of $Y-Y$ or of $Y'-Y'$, and g^{YY} that of $Y_i-Y'_j$ with $i\neq j$. $\varDelta$ indicates a small deviation from the equilibrium value. α's refer to the bond angles such as $\angle X'XY$ or $\angle XX'Y'$ and β's to $\angle YXY$ or $\angle Y'X'Y'$. As seen easily from Fig. 1 the redundant condition is given by

$$\sum(\varDelta\phi_{ij})=0,\tag{2}$$

and the four relations

$$\begin{aligned}\varDelta R:\quad&{K'}_{XX}R+6{F'}_{XY}(R-r\cos\alpha)\\&\quad+6{J'}_{YY}(R-2r\cos\alpha)=0,\end{aligned}\tag{3a}$$

$$\begin{aligned}\varDelta r:\quad&{K'}_{XY}r+{F'}_{XY}(r-R\cos\alpha)\\&+2{F'}_{YY}r(1-\cos\beta)\\&+2{J'}_{YY}[r(1/2+3/2\cos^2\alpha)-R\cos\alpha]=0,\end{aligned}\tag{3b}$$

$$\begin{aligned}\varDelta\alpha:\quad&{H'}_{XXY}R+3{H'}_{YXY}r\sin\alpha\cos\alpha/\sin\beta\\&+2{J'}_{YY}(R\sin\alpha-3/2\,r\sin\alpha\cos\alpha)\\&+{F'}_{XY}R\sin\alpha+3{F'}_{YY}r\sin\alpha\cos\alpha=0,\end{aligned}\tag{3c}$$

and

$$\begin{aligned}\varDelta\phi:\quad&(\kappa+\Phi')+\sqrt{3}\,{H'}_{YXY}\sin^2\alpha/\sin\beta\\&+\sqrt{3}\,{F'}_{YY}\sin^2\alpha+\sqrt{3}/2{J'}_{YY}\sin^2\alpha=0\end{aligned}\tag{3d}$$

must be fulfilled to secure the stable equilibrium. These four types of coodinates are taken to be independent; that is, two distances, $X-X'(\varDelta R)$ and $X-Y(\varDelta r)$, and two angles, $\angle X'XY(\varDelta\alpha)$ and $\varDelta\phi$. On the other hand angles $\angle YXY(\varDelta\beta)$ are dependent coordinates and can be expressed in terms of $\varDelta\alpha$ and $\varDelta\phi$. It is a quite conspicuous difference to the usual treatment. κ is the Lagrange's multiplication factor which is used to take into consideration the redundant condition of Eq. 2.

There are eight coefficients in the linear terms, but only four of them are independent, owing to the four relations given above. These four independent coefficients and the eight force constants in the quadratic expression are the parameters available for making the calculated frequencies agree with the observed ones.

If the molecule has the staggered configuration, as is usually the case, the

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11) Y. Morino and E. Hirota, ibid 28, 185 (1958).

12) See ref. 9. Recently an additional degree of freedom was introduced; that is, the bending about the middle point of the X-X bond, cf. T. Shimanouchi, *J. Chem. Phys.* **26**, 594 (1957).

molecular symmetry is D_{3d} and the normal modes are factored into five groups; three modes belong to A_{1g}, one to A_{1u}, two to A_{2u}, three pairs to E_g, and the last three ones to E_u. The symmetry coordinates are given by

$$\mathrm{A}_{1g}\quad\begin{cases} S_1=1/\sqrt{6}\,[\Delta r_1+\Delta r_2+\Delta r_3+\Delta r'_1\\ \qquad +\Delta r'_2+\Delta r'_3],\\ S_2=\Delta R,\\ S_3=r/\sqrt{6}\,[\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3+\Delta\alpha'_1\\ \qquad +\Delta\alpha'_2+\Delta\alpha'_3],\\ S_{13}=r/\sqrt{6}\,[\Delta\phi_{12}+\Delta\phi_{23}+\Delta\phi_{31}\\ \qquad +\Delta\phi_{21}+\Delta\phi_{32}+\Delta\phi_{13}],\end{cases}\tag{4a}$$

$$\mathrm{A}_{1u}\quad \begin{aligned} S_4=r/\sqrt{6}\,[&\Delta\phi_{12}+\Delta\phi_{23}+\Delta\phi_{31}\\ &-\Delta\phi_{21}-\Delta\phi_{32}-\Delta\phi_{13}],\end{aligned}\tag{4b}$$

$$\mathrm{A}_{2u}\quad\begin{cases} S_5=1/\sqrt{6}\,[\Delta r_1+\Delta r_2+\Delta r_3\\ \qquad -\Delta r'_1-\Delta r'_2-\Delta r'_3],\\ S_6=r/\sqrt{6}\,[\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3\\ \qquad -\Delta\alpha'_1-\Delta\alpha'_2-\Delta\alpha'_3],\end{cases}\tag{4c}$$

$$\mathrm{E}_g\quad\begin{cases} S_{7a}=1/2[\Delta r_1-\Delta r_3+\Delta r'_1-\Delta r'_3],\\ S_{7b}=1/2\sqrt{3}\,[\Delta r_1-2\Delta r_2+\Delta r_3\\ \qquad +\Delta r'_1-2\Delta r'_2+\Delta r'_3],\\ S_{8a}=r/2[\Delta\alpha_1-\Delta\alpha_3+\Delta\alpha'_1-\Delta\alpha'_3],\\ S_{8b}=r/2\sqrt{3}\,[\Delta\alpha_1-2\Delta\alpha_2+\Delta\alpha_3\\ \qquad +\Delta\alpha'_1-2\Delta\alpha'_2+\Delta\alpha'_3],\\ S_{9a}=r/2[\Delta\phi_{12}-\Delta\phi_{23}+\Delta\phi_{21}-\Delta\phi_{32}],\\ S_{9b}=r/2\sqrt{3}\,[-\Delta\phi_{12}-\Delta\phi_{23}+2\Delta\phi_{31}\\ \qquad -\Delta\phi_{21}-\Delta\phi_{32}+2\Delta\phi_{13}],\end{cases}\tag{4d}$$

$$\mathrm{E}_u\quad\begin{cases} S_{10a}=1/2[\Delta r_1-\Delta r_3-\Delta r'_1+\Delta r'_3],\\ S_{10b}=1/2\sqrt{3}\,[\Delta r_1-2\Delta r_2+\Delta r_3\\ \qquad -\Delta r'_1+2\Delta r'_2-\Delta r'_3],\\ S_{11a}=r/2[\Delta\alpha_1-\Delta\alpha_3+\Delta\alpha'_1-\Delta\alpha'_3],\\ S_{11b}=r/2\sqrt{3}\,[\Delta\alpha_1-2\Delta\alpha_2+\Delta\alpha_3\\ \qquad -\Delta\alpha'_1+2\Delta\alpha'_2-\Delta\alpha'_3],\\ S_{12a}=r/2\sqrt{3}\,[\Delta\phi_{12}+\Delta\phi_{23}-2\Delta\phi_{31}\\ \qquad -\Delta\phi_{21}-\Delta\phi_{32}+2\Delta\phi_{13}],\\ S_{12b}=r/2[\Delta\phi_{12}-\Delta\phi_{23}-\Delta\phi_{21}+\Delta\phi_{32}].\end{cases}\tag{4e}$$

S_{13} is obviously a redundant coordinate and can be ignored hereafter. S_4 corresponds to the torsional oscillation and is split by the present molecular symmetry from other symmetry coordinates. The torsional coordinate is, in general, not split from others, hence the coupling between the internal rotation and other normal modes becomes more appreciable in molecules of lower symmetry. For the ethane-type molecules the coupling is indirect: as shown in the following discussion the force constants J_{YY} and Φ introduced above enter not only in the F-matrix of A_{1u} but also in the F-matrix of other symmetries.

The unitary transformation given by Eqs. 4 factorizes also the potential energy of Eq. 1 into five parts, which are expressed by the following five F-matrices:

$$\mathrm{F}(\mathrm{A}_{1g})=\begin{bmatrix} A+2B+2B' & & \\ \sqrt{6}C & A' & \\ D+2D'+2D'' & \sqrt{6}D_0 & L+2L'+2L'' \end{bmatrix}\tag{5a}$$

$$\mathrm{F}(\mathrm{A}_{1u})=[N-2N']\tag{5b}$$

$$\mathrm{F}(\mathrm{A}_{2u})=\begin{bmatrix} A+2B-2B' & \\ D+2D'+2D'' & L+2L'-2L'' \end{bmatrix}\tag{5c}$$

$$\mathrm{F}(\mathrm{E}_g)=\begin{bmatrix} A-B-B' & & \\ D-D'-D'' & L-L'-L'' & \\ E-2E' & M-2M' & N-N' \end{bmatrix}\tag{5d}$$

$$\mathrm{F}(\mathrm{E}_u)=\begin{bmatrix} A-B+B' & & \\ D-D'+D'' & L-L'+L'' & \\ \sqrt{3}E & \sqrt{3}M & N+N' \end{bmatrix}\tag{5e}$$

where the notations A, B, and so on are given in Fig. 2. The potential energy of the internal rotation in the present type molecule is safely assumed as $V=(V_0/2)(1-\cos 3\phi)$, which, in the high barrier approximation, can be expanded as $(9V_0/4)\phi^2$. The internal coordinate ϕ is expressed in terms of the symmetry coordinate S_4; $\phi=(1/\sqrt{6}r)S_4$, and the expression for the potential energy becomes $(3V_0/8r^2)S_4^2$, which is put equal to $(1/2)F_{44}S_4^2$, thus

$$\begin{aligned}\mathrm{F}(\mathrm{A}_{1u})&=(3/4)(V_0/r^2)\\ &=\Phi+(3/4)J_{YY}r^2\sin^4\alpha/(g^{YY})^2\\ &\quad-(1/2)J'_{YY}[\sin^2\alpha\\ &\quad+3r^2\sin^4\alpha/2(g^{YY})^2],\end{aligned}\tag{6}$$

$\mathrm{F}(\mathrm{A}_{1u})$ being equal to F_{44}. It is an important relation giving V_0 in terms of the two force constants J_{YY} and Φ. It is to be noted that the two force constants, J_{YY} and Φ, important for the internal rotation enter also in the F-matrices of A_{1g}, E_g and E_u symmetries. Hence the internal rotation couples indirectly with other normal modes through J_{YY} and Φ.

The kinetic energy matrices are also factorized analogously; tedious calculation gives:

$$\begin{aligned}
A={}&K_{XY}+F_{XY}(r-R\cos\alpha)^2/q^2_{XY}+2F_{YY}r^2(1-\cos\beta)^2/q^2_{YY}+2J_{YY}[r(1+3\cos^2\alpha)/2\\
&-R\cos\alpha]^2/(g^{YY})^2+F'_{XY}[1-(r-R\cos\alpha)^2/q^2_{XY}]+2F'_{YY}[1-r^2(1-\cos\beta)^2/q^2_{YY}]\\
&+2J'_{YY}\{1-[r(1+3\cos^2\alpha)/2-R\cos\alpha]^2/(g^{YY})^2\},
\end{aligned}$$

$$B=F_{YY}r^2(1-\cos\beta)^2/q^2_{YY}-F'_{YY}[\cos\beta+r^2(1-\cos\beta)^2/q^2_{YY}],$$

$$\begin{aligned}
B'={}&J_{YY}[r(1+3\cos^2\alpha)/2-R\cos\alpha]^2/(g^{YY})^2+J'_{YY}\{(-1+3\cos^2\alpha)/2-[r(1+3\cos^2\alpha)/2\\
&-R\cos\alpha]^2/(g^{YY})^2\},
\end{aligned}$$

$$\begin{aligned}
C={}&F_{XY}(R-r\cos\alpha)(r-R\cos\alpha)/q^2_{XY}+2J_{YY}[r(1+3\cos^2\alpha)/2-R\cos\alpha]\\
&\times(R-2r\cos\alpha)/(g^{YY})^2-F'_{XY}[\cos\alpha+(R-r\cos\alpha)(r-R\cos\alpha)/q^2_{XY}]-2J'_{YY}\{\cos\alpha\\
&+[r(1+3\cos^2\alpha)/2-R\cos\alpha](R-2r\cos\alpha)/(g^{YY})^2\},
\end{aligned}$$

$$\begin{aligned}
A'={}&K_{XY}+6F_{XY}(R-r\cos\alpha)^2/q^2_{XY}+6J_{YY}(R-2r\cos\alpha)^2/(g^{YY})^2\\
&+6F'_{XY}[1-(R-r\cos\alpha)^2/q^2_{XY}]+6J'_{YY}[1-(R-2r\cos\alpha)^2/(g^{YY})^2],
\end{aligned}$$

$$\begin{aligned}
D={}&F_{XY}r(r-R\cos\alpha)\sin\alpha/q^2_{XY}+3F_{YY}r^3(1-\cos\beta)\sin\alpha\cos\alpha/Rq^2_{YY}+2J_{YY}(1/R)\\
&\times[r(1+3\cos^2\alpha)/2-R\cos\alpha][Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]/(g^{YY})^2+F'_{XY}[\sin\alpha-r\\
&\times(r-R\cos\alpha)\sin\alpha/q^2_{XY}]+3F'_{YY}[(r/R)-r^3(1-\cos\beta)/Rq^2_{YY}]\sin\alpha\cos\alpha+2J'_{YY}(1/R)\\
&\times\{R\sin\alpha-(3/2)r\sin\alpha\cos\alpha-[r(1+3\cos^2\alpha)/2-R\cos\alpha]\\
&\times[Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]/(g^{YY})^2\},
\end{aligned}$$

$$\begin{aligned}
D'={}&(3/2)F_{YY}r^3(1-\cos\beta)\sin\alpha\cos\alpha/Rq^2_{YY}+(3/2)F'_{YY}\\
&\times[(r/R)-r^3(1-\cos\beta)/Rq^2_{YY}]\sin\alpha\cos\alpha,
\end{aligned}$$

$$\begin{aligned}
D''={}&J_{YY}(1/R)[r(1+3\cos^2\alpha)/2-R\cos\alpha][Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]/(g^{YY})^2\\
&-J'_{YY}(1/R)\{(3/2)r\sin\alpha\cos\alpha+[r(1+3\cos^2\alpha)/2-R\cos\alpha]\\
&\times[Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]/(g^{YY})^2,
\end{aligned}$$

$$\begin{aligned}
D_0={}&F_{XY}r(R-r\cos\alpha)\sin\alpha/q^2_{XY}+2J_{YY}(1/R)[R-2r\cos\alpha][Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]/(g^{YY})^2\\
&+F'_{XY}[r\sin\alpha/R-r(R-r\cos\alpha)\sin\alpha/q^2_{XY}]+2J'_{YY}(1/R)\{r\sin\alpha-[R-2r\cos\alpha][Rr\sin\alpha\\
&-(3/2)r^2\sin\alpha\cos\alpha]/(g^{YY})^2\},
\end{aligned}$$

$$\begin{aligned}
L={}&H_{XXY}+(9/2)H_{YXY}(r/R)^2\sin^2\alpha\cos^2\alpha/\sin^2\beta+F_{XY}r^2\sin^2\alpha/q^2_{XY}+(9/2)F_{YY}(r^2/R)^2\\
&\times\sin^2\alpha\cos^2\alpha/q^2_{YY}+2J_{YY}(1/R)^2[Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]^2/(g^{YY})^2\\
&+2H'_{YXY}(r/R)^2(\cos\beta/\sin^3\beta)[\sin^2\beta-(9/4)\sin^2\alpha\cos^2\alpha]+F'_{XY}[r\cos\alpha/R-r^2\sin^2\alpha/q^2_{XY}]\\
&+2F'_{YY}(r/R)^2[\cos\beta-(9/4)r^2\sin^2\alpha\cos^2\alpha/q^2_{YY}]+2J'_{YY}(1/R^2)\{[Rr\cos\alpha-r^2(-1\\
&+3\cos^2\alpha)/2]-[Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha]^2/(g^{YY})^2\},
\end{aligned}$$

$$\begin{aligned}
L'={}&(9/4)H_{YXY}(r/R)^2\sin^2\alpha\cos^2\alpha/\sin^2\beta+(9/4)F_{YY}(r^2/R)^2\sin^2\alpha\cos^2\alpha/q^2_{YY}\\
&+H'_{YXY}(r/R)^2(2\sin^2\beta\cos^2\alpha-4\sin^2\beta\sin^2\alpha-9\cos\beta\sin^2\alpha\cos^2\alpha)/4\sin^3\beta\\
&+F'_{YY}(r^2/2R^2)[\cos^2\alpha-2\sin^2\alpha-qr^2\sin^2\alpha\cos^2\alpha/2q^2_{YY}],
\end{aligned}$$

$$\begin{aligned}
L''={}&J_{YY}(1/R^2)(Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha)^2/(g^{YY})^2+J'_{YY}(1/R^2)\{r^2(\sin^2\alpha-(1/2)\cos^2\alpha)\\
&-(Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha)^2/(g^{YY})^2\},
\end{aligned}$$

$$\begin{aligned}
N={}&\Phi+(3/2)H_{YXY}\sin^4\alpha/\sin^2\beta+(3/2)F_{YY}r^2\sin^4\alpha/q^2_{YY}+(3/4)J_{YY}r^2\sin^4\alpha/(g^{YY})^2\\
&-H'_{YXY}(3\cos\beta\sin^4\alpha+2\sin^2\beta\sin^2\alpha)/2\sin^3\beta-F'_{YY}\sin^2\alpha(1+3r^2\sin^2\alpha/2q^2_{YY})\\
&-J'_{YY}[\sin^2\alpha/2+3r^2\sin^4\alpha/4(g^{YY})^2],
\end{aligned}$$

$$\begin{aligned}
N'={}&(3/4)H_{YXY}\sin^4\alpha/\sin^2\beta+(3/4)F_{YY}r^2\sin^4\alpha/q^2_{YY}-H'_{YXY}(3\cos\beta\sin^4\alpha\\
&+2\sin^2\beta\sin^2\alpha)/4\sin^3\beta-(1/2)F'_{YY}\sin^2\alpha(1+3r^2\sin^2\alpha/2q^2_{YY}),
\end{aligned}$$

$$\begin{aligned}
E={}&(\sqrt{3}/2)F_{YY}r^2(1-\cos\beta)\sin^2\alpha/q^2_{YY}+(\sqrt{3}/2)J_{YY}r[r(1+3\cos^2\alpha)/2-R\cos\alpha]\sin^2\alpha/(g^{YY})^2\\
&+(\sqrt{3}/2)F'_{YY}[1-r^2(1-\cos\beta)/q^2_{YY}]\sin^2\alpha+(\sqrt{3}/2)J'_{YY}\{1-r[r(1+3\cos^2\alpha)/2\\
&-R\cos\alpha]/(g^{YY})^2\}\sin^2\alpha,
\end{aligned}$$

$$E'=(\sqrt{3}/2)F_{YY}r^2(1-\cos\beta)\sin^2\alpha/q^2_{YY}+(\sqrt{3}/2)F'_{YY}[1-r^2(1-\cos\beta)/q^2_{YY}]\sin^2\alpha,$$

$$\begin{aligned}
M={}&(3\sqrt{3}/4)H_{YXY}(r/R)\sin^3\alpha\cos\alpha/\sin^2\beta+(3\sqrt{3}/4)F_{YY}(r^3/R)\sin^3\alpha\cos\alpha/q^2_{YY}\\
&+(\sqrt{3}/2)J_{YY}(r^2/R)\sin^2\alpha(Rr\sin\alpha-(3/2)r^2\sin\alpha\cos\alpha)/(g^{YY})^2\\
&+(\sqrt{3}/4)H'_{YXY}(r/R)\sin\alpha\cos\alpha(2\sin^2\beta-3\cos\beta\sin^2\alpha)/\sin^3\beta+(\sqrt{3}/2)\\
&\times F'_{YY}(r/R)\sin\alpha\cos\alpha(1-3r^2\sin^2\alpha/2q^2_{YY})+(\sqrt{3}/2)J'_{YY}(r/R)\sin\alpha[\cos\alpha\\
&-(Rr\sin\alpha-(1/2)r^2\sin\alpha\cos\alpha)\sin\alpha/(g^{YY})^2],
\end{aligned}$$

$$\begin{aligned}
M'={}&(3\sqrt{3}/4)H_{YXY}(r/R)\sin^3\alpha\cos\alpha/\sin^2\beta+(3\sqrt{3}/4)F_{YY}(r^3/R)\sin^3\alpha\cos\alpha/q^2_{YY}\\
&+(\sqrt{3}/4)H'_{YXY}(r/R)\sin\alpha\cos\alpha(2\sin^2\beta-3\cos\beta\sin^2\alpha)/\sin^3\beta\\
&+(\sqrt{3}/2)F'_{YY}(r/R)\sin\alpha\cos\alpha(1-3r^2\sin^2\alpha/2q^2_{YY})
\end{aligned}$$

Fig. 2. Notations used for the elements of the F-matrix.

$$A=\mu_1+\mu_2,\qquad B=\mu_1\cos\beta,\qquad C=\mu_1\operatorname{con}\alpha,$$
$$C_0=2\mu_1,\qquad D=D''=-\mu_1\rho\sin\alpha,$$
$$D'=-\mu_1[(\rho-\cos\alpha)\cos\beta+(1-\rho\cos\alpha)\cos\alpha]/\sin\alpha,$$
$$D'''=(1/2)\mu_1\rho\sin\alpha,\qquad D_0=-\mu_1\sin\alpha,$$
$$L=\mu_1[2\rho^2-2\rho\cos\alpha+1]+\mu_2,$$
$$L'=\mu_1[(2\rho^2-2\rho\cos\alpha+\cos^2\alpha)\cos\beta-2(1-\rho\cos\alpha+\rho^2)\cos^2\alpha+1]/\sin^2\alpha$$
$$L''=2\mu_1\rho(\rho-\cos\alpha),\qquad L'''=-\mu_1\rho(\rho-\cos\alpha),$$
$$N=2\mu_1[1-3\rho\cos\alpha+3\rho^2\cos^2\alpha]/\sin^2\alpha+2\mu_2[5-9\cos^2\alpha-4\cos\beta]/3\sin^4\alpha,$$
$$N'=\mu_1[2(1-6\cos^2\alpha)-9\rho\cos\alpha(1-5\cos^2\alpha)+9\rho^2\cos^2\alpha(1-5\cos^2\alpha)+2(5-18\rho\cos\alpha$$
$$+18\rho^2\cos^2\alpha)\cos\beta]/3\sin^4\alpha,$$
$$N''=\mu_1[2(4-9\cos^2\alpha)-36\rho\cos\alpha(1-2\cos^2\alpha)+36\rho^2\cos^2\alpha(1-2\cos^2\alpha)+2(5$$
$$-18\rho\cos\alpha+18\rho^2\cos^2\alpha)\cos\beta]/3\sin^4\alpha,$$
$$N'''=\mu_1[1-6\cos^2\alpha+18\rho\cos^3\alpha-18\rho^2\cos^4\alpha+(5-18\rho\cos\alpha+18\rho^2\cos^2\alpha)\cos\beta]/3\sin^4\alpha$$
$$+\mu_2(-1-3\cos^2\alpha+4\cos\beta)/3\sin^4\alpha,$$
$$E=-(\sqrt{3}/2)\mu_1\rho\cos\alpha,$$
$$E'=(1/\sqrt{3})(\mu_1/\sin^2\alpha)[(1-3\rho\cos\alpha)\cos\beta-(1-(3/2)\rho\cos\alpha-(3/2)\rho\cos^3\alpha)],$$
$$E''=(1/\sqrt{3})(\mu_1/\sin^2\alpha)[(1-3\rho\cos\alpha)\cos\beta+(2-3\cos^2\alpha)-3\rho\cos\alpha(1-2\cos^2\alpha)],$$
$$M=-(\sqrt{3}/2)(\mu_1\rho/\sin\alpha)(1+\cos^2\alpha-2\rho\cos\alpha),$$
$$M'=(1/\sqrt{3})(\mu_1/\sin^3\alpha)[(\cos\alpha-3\rho-3\rho\cos^2\alpha+6\rho^2\cos\alpha)\cos\beta+(-\cos\alpha+(3/2)\rho$$
$$+3\rho\cos^2\alpha+(3/2)\rho\cos^4\alpha-3\rho^2\cos\alpha-3\rho^2\cos^3\alpha)],$$
$$M''=(1/\sqrt{3})(\mu_1/\sin^3\alpha)[(\cos\alpha-3\rho-3\rho\cos^2\alpha+6\rho^2\cos\alpha)\cos\beta+(2\cos\alpha-3\cos^3\alpha$$
$$-3\rho+3\rho\cos^2\alpha+6\rho\cos^4\alpha+6\rho^2\cos\alpha-12\rho^2\cos^3\alpha)]$$

where

$$\mu_1=1/m_C,\quad \mu_2=1/m_{Cl},\quad \rho=r/R.$$

Fig. 3. Notations used for the elements of the G-matrix.

$$G(A_{1g})=\begin{bmatrix} A+2B & & \\ \sqrt{6}C & C_0 & \\ D+2D'+D''+2D''' & \sqrt{6}D_0 & L+2L'+L''+2L''' \end{bmatrix} \tag{7a}$$

$$G(A_{1u})=[N+2N'-N''-2N'''] \tag{7b}$$

$$G(A_{2u})=\begin{bmatrix} A+2B & \\ D+2D'-D''-2D''' & L+2L'-L''-2L''' \end{bmatrix} \tag{7c}$$

$$G(E_g)=\begin{bmatrix} A-B & & \\ D-D'+D''-D''' & L-L'+L''-L''' & \\ E-2E'+E'' & M-2M'+M'' & N-N'+N''-N''' \end{bmatrix} \tag{7d}$$

$$G(E_u)=\begin{bmatrix} A-B & & \\ D-D'-D''+D''' & L-L'-L''+L''' & \\ \sqrt{3}(E-E'') & \sqrt{3}(M-M'') & N-N'-N''+N''' \end{bmatrix} \tag{7e}$$

where the notations A, B, and so on are given in Fig. 3. Using the **F**-matrices Eqs. 5 and the **G**-matrices Eqs. 7 the frequencies of normal modes can be calculated through the determinant[13]:

$$|\,\mathbf{GF}-\lambda\mathbf{E}\,|=0 \tag{8}$$

where **E** denotes the unit matrix.

A Numerical Example; Hexachloroethane

One of the molecules, to which the present treatment can adequately be applied, is hexachloroethane, for a rather large steric repulsion is expected for the large substituents, chlorine atoms, and seems to result in a high hindering potential barrier. In fact, according to an electron diffraction investigation by Morino and Iwasaki[14], the barrier height of 15 kcal/mole was reported, definitely higher than the level of thermal energy of about 600 cal/mole. Hence, the high barrier approximation is expected in this case.

By using Eqs. 5, 7, and 8 with appropriate force constants given in Table

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[13] E. Bright Wilson, Jr., ibid. **7**, 1047 (1939); **9**, 76 (1941).

[14] Y. Morino and M. Iwasaki ibid. **17**, 216 (1949).

TABLE I

FORCE CONSTANTS USED FOR HEXACHLOROETHANE (in 10^5 dynes/cm).

$K_{CC}=2.15$, $F_{CCl}=0.55$, $F'_{CCl}=-0.04$, $H_{CCCl}=0.07$, $K_{CCl}=2.30$, $F_{ClCl}=0.70$, $F'_{ClCl}=-0.035$, $H_{ClCCl}=0.04$, $J_{ClCl}=0.090$, others assumed to be zero

TABLE II

CALCULATED AND OBSERVED FREQUENCIES OF NORMAL VIBRATIONS OF HEXACHLOROETHANE (in cm^{-1}).

		$\tilde{\nu}_{calc}$	$\tilde{\nu}_{obs}$	deviation(%)
A_{1g}	ν_1	969	974	− 0.6
	ν_2	469	431	+ 8.9
	ν_3	189	169	+12.0
A_{1u}	ν_4	62	—	—
A_{2u}	ν_5	671	675	− 0.6
	ν_6	354	—	—
E_g	ν_7	851	853	− 0.3
	ν_8	313	341	− 8.2
	ν_9	200	224	−10.6
E_u	ν_{10}	799	769	+ 3.9
	ν_{11}	249	—	—
	ν_{12}	143	—	—

TABLE III

CALCULATED AND OBSERVED ROOT MEAN SQUARE AMPLITUDES OF HEXACHLOROETHANE (in Å)

atom pair	calc.	obs.
C—C	0.055	—
C—Cl	0.051	0.06_6
C...Cl	0.071	0.06_9
Cl...Cl	0.070	0.06_4
*g*Cl...Cl	(0.136)	0.13_6
*t*Cl...Cl	0.069	0.10_9

I the frequencies of twelve normal vibrations were calculated; the results are summarized in Table II, where the observed data, if available, are given for comparison. It is seen that the discrepancy is somewhat large for ν_3 and ν_9; one is too high (+12.0%) and the other is too low (−10.6%). However, it was found difficult to make better the agreements of both frequencies simultaneously. Apart from this point, the set of force constants is satisfactory, though the low frequency vibrations active in the infrared have not yet been observed. (ν_6 of A_{2u} type and ν_{11} and ν_{12} of E_u type). Unfortunately all these bands are of low frequency and have large contributions to the root mean square amplitudes, so that the accuracies of the calculated root mean square amplitudes are limited.

The force constant J_{YY} was chosen to be $0.090 \cdot 10^5$ dynes/cm, which means the potential barrier of about 10 kcal/mole (see Eq. 6), and the frequency of the torsional mode was calculated to be 62 cm^{-1}. These values are chosen because they are consistent with the result of the recent electron diffraction experiment[11] (see the next section). Another force constant Φ was simply set equal to zero, for the interaction between chlorine atoms was considered to be more important than the C—Cl bond interactions.

The **L**-matrices given by the relation $\mathbf{S}=\mathbf{LQ}$ are important not only for understanding the nature of the normal modes, but also for calculating the mean amplitudes. The following values were obtained for the elements of the **L**-matrices;

$$A_{1g} \begin{bmatrix} +0.179 & +0.154 & +0.011 \\ -0.407 & +0.032 & -0.001 \\ +0.469 & -0.048 & +0.167 \end{bmatrix} \tag{9a}$$

$$A_{1u} \ [+0.356] \tag{9b}$$

$$A_{2u} \begin{bmatrix} +0.232 & -0.047 \\ +0.399 & +0.301 \end{bmatrix} \tag{9c}$$

$$E_g \begin{bmatrix} +0.369 & +0.054 & +0.018 \\ -0.889 & +0.287 & +0.144 \\ +1.090 & -0.432 & +0.186 \end{bmatrix} \tag{9d}$$

$$E_u \begin{bmatrix} +0.373 & +0.003 & -0.013 \\ -0.099 & +0.006 & +0.176 \\ -0.335 & +0.239 & +0.054 \end{bmatrix} \tag{9e}$$

where the unit is $(a.m.u.)^{-1/2}$. It can be seen that the coupling between the bond stretching modes and the bond angle deformation vibrations is unusually large.

Mean Amplitudes and Determination of the Potential Barrier

The recent improvement in the electron diffraction technique, the sector-microphotometer method, gives us not only the equilibrium distances of atom pairs but also their mean square amplitudes $<\Delta r^2_{ij}>_{AV}$[15]. Because Δr_{ij}, the small deviation from the equilibrium distance of atom pair (i, j), is one of the internal coordinates, it can be expressed in terms of the normal coordinates Q_k's:

$$\Delta \mathbf{r}=\mathbf{AULQ} \tag{10}$$

where **U** and **L** are the unitary and the **L**-matrices, as explained above, and **A** is a matrix which transforms the independent internal coordinates to a particular atom distance, for example between the two atom pair (i, j). Thus the mean amplitude $<\Delta r^2_{ij}>_{AV}$ is given by

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[15] I. L. Karle and J. Karle, ibid. **17**, 1052 (1949).

$$<\Delta r^2_{ij}>_{AV} = \mathbf{AUL} <\mathbf{Q}^2>_{AV} \mathbf{L'U'A'} \quad (11)$$

where $<\mathbf{Q}^2>_{AV}$ is the square of the normal coordinate averaged out over its vibrational states and is for the kth vibration given by

$$<Q^2_k>_{AV} = (\boldsymbol{h}/8\pi^2\nu_k)\coth(\boldsymbol{h}\nu_k/2\boldsymbol{k}T). \quad (12)$$

For hexachloroethane there are six atom pairs and their mean amplitudes have been observed except for the C—C atom pair which has too low scattering power to be measured accurately. Thus it is very interesting to compare these observed data with the calculated values based upon Eqs. 11 and 12. The agreement between them, though indirectly, indicates the validity of the force field we have applied. As shown in Table III, the agreement is very good when the experimental error and the approximation made for the force field are taken into consideration.

One atom pair, denoted as gCl—Cl in Table III, is particularly important for the determination of the potential barrier. The mean amplitude of the atom pair is also expressed by a sum of the mean square amplitudes of several normal vibrations, including that of the torsional oscillation, Q_4. If the classical approximation of Eq. (12) is applied for the torsional mode*, the mean amplitude of the gCl—Cl atom pair is given by

$$<r^2(g\mathrm{Cl{-}Cl})>_{AV} = A + B/V_0, \quad (13)$$

where the first term A is the contribution from skeletal vibrations and the second term B/V_0 from the torsional mode, and the constant B is given by

$$B = (2/9)\boldsymbol{k}T(r^4/(g^{\mathrm{ClCl}})^2)\sin^4\alpha\sin^2\phi. \quad (14)$$

However, since the electron diffraction experiment gives us only this sum and cannot separate two parts, it is impossible to obtain the value of the potential barrier only by the observation. Now, since a good force field has become available for us, the unknown constant A can be calculated to be $11.53\cdot10^{-3}$ Å^2. Thus the observed mean amplitude $<r^2(g\mathrm{Cl{-}Cl})>_{AV}$ determines the barrier height V_0. A remark must, however, be given to the value of A, which is indirectly a function of V_0, for the force constant J_{ClCl} determining V_0 enters also into the **F**-matrices of skeletal modes. The force constants given in Table I and the value of A shown above are all consistent with the final value of V_0 of about 10.8 kcal/mole. As described above, the force constants were able to reproduce the observed frequencies of normal vibrations with error of 10%, thus the uncertainties of the calculated mean square amplitudes are about 20% or less, and the height of potential barrier is also accurate in the same order of magnitude.

Discussion

The force field developed here is only of an approximate nature, hence the values of individual force constants given in Table I do not reflect exactly the interatomic interactions in molecules; other coupling constants omitted in the present investigation may influence strongly the values of force constants. It is, however, interesting to discuss the force constant J_{ClCl} introduced first in the present paper, for this constant determines the frequency of the torsional oscillation. The torsional mode is the only one belonging to the A_{1u} symmetry, hence the value of J_{ClCl} is relatively independent of the non-diagonal coupling constants in the **F**-matrices. In fact the constant J_{ClCl} plays the main role in the **F**-matrix of the A_{1u} symmetry [cf. Eq. 5b]. As stated above, its value can be determined by the recent electron diffraction experiment accurately enough to make it worth while to discuss further.

The origin of the hindrance of the internal rotation is very complicated; the diversity of the circumstances has already been noted in the Introduction. Lassettre and Dean[16] discussed the effect of the bond quadrupole interaction. In many instances this effect would be appreciable[17], but the steric repulsion is more important in the present example of hexachloroethane; if one considers the cis-configuration of this molecule the distance between the two eclipsed chlorine atoms becomes about 2.72 Å, and the exchange force would be very large. Morino and Miyagawa[18] gave a semi-empirical expression for the repulsive potential between two chlorine atoms:

$$V = -1.515\cdot10^{-10}r^{-6} + 1.620\cdot10^{-7}r^{-12} \quad \text{erg/molecule,} \quad (15)$$

r being given in unit of Å. It is based

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* The frequency of the torsion Q_4 is low, which allows us to treat it classically.

[16] E. N. Lassettre and L. B. Dean, Jr., *J. Chem. Phys.* **17**, 317 (1949); L. J. Oosterhoff, *Discussions Faraday Soc.* **10**, 79 (1951).

[17] H. S. Gutowsky and E. O. Stejskal, *J. Chem. Phys.* **22**, 937 (1954); D. R. Lide and D. K. Coles, *Phys. Rev.* **80**, 911 (1950) and so on; see also ref. 11.

[18] Y. Morino and I. Miyagawa, *J. Chem. Soc. Japan*, (*Nippon Kagaku Zassi*) **68**, 62 (1947).

upon the potential obtained from the second virial coefficient of chlorine gas. The force constant J_{ClCl} corresponds to the second derivative of this potential at the equilibrium distance of gCl—Cl pair:

$$J_{\text{ClCl}} = (\partial^2 V/\partial r^2)_{r=g\text{ClCl}}, \qquad (16)$$

which is calculated to be $0.17 \cdot 10^5$ dynes/cm, which is in the same order of magnitude with but about twice as large as that previously given in Table I.

The high barrier approximation was used through this paper, but the anharmonicity may be appreciable for the internal rotation. It is, however, of the order of magnitude of $(h\nu_4)^2/V_0$, which is very small, and can be neglected in the present discussion. If the barrier height becomes lower, each torsional level splits owing to the symmetry of the two CCl_3 groups; the three states $H^n{}_1$, $H^n{}_2$ and $H^n{}_3$ corresponding to the three minima and degenenerating in the high barrier case, must be replaced by the irreducible representation[3,5]:

$$\Psi^n{}_1 = (1/3)^{1/2} \exp(-iK\phi/2)(H^n{}_1 + H^n{}_2 + H^n{}_3), \qquad (17a)$$

$$\Psi^n{}_2 = (1/6)^{1/2} \exp(-iK\phi/2)(2H^n{}_1 - H^n{}_2 - H^n{}_3), \qquad (17b)$$

and $$\Psi^n{}_3 = (1/2)^{1/2} \exp(-iK\phi/2)(H^n{}_2 - H^n{}_3), \qquad (17c)$$

but this splitting due to the tunneling effect is also small and can be ignored in the present case.

The projected angle introduced here may be applied as one of the internal coordinates to other molecules of lower symmetries with the internal rotation of relatively high frequencies; the mathematical complexity involved is not very serious. If the internal rotation is included in this way in the treatment of the normal mode, its important coupling with other normal vibrations of low frequencies will be obtained, and also the more correct force constants for the latter modes.

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