POTENTIAL CONSTANTS OF ETHYLENE OXIDE, ETHYLENE OXIDE-$d_4$ AND ETHYLENE SULPHIDE

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1. INTRODUCTION

The possible structure of ethylene oxide (C$_2$H$_4$O) molecule is that the O and the two C atoms form an isosceles triangle and the two CH$_2$ groups form planes at right angles to the C$_2$O plane. Under this assumption, the molecule belongs to the point group C$_2v$ and the number of fundamental frequencies is fifteen. Of these fifteen fundamentals, five are of A$_1$ type, three of A$_2$ type, four of B$_1$ type and three of B$_2$ type. The fundamentals of the A$_2$ species are inactive in infra-red but active in Raman effect. The fundamentals of the other three species are active in both infra-red and Raman spectra.

The vibrational spectrum of ethylene oxide has been measured by a number of authors. Lord and Nolin$^2$ have studied the infra-red and Raman spectra of ethylene oxide and also of its deuterium analogue and have made an assignment of the observed fundamentals. Their assignment correlates well with that of the analogous molecules, cyclopropane and cyclopropane-$d_4$.

Gunthard et al.$^3$ have calculated three force constants of ethylene oxide molecule by assuming a simple valence force field and making use only of the A$_2$ and B$_2$ type frequencies. Stone$^4$ has used a generalised valence force field and has evaluated ten force constants taking into account the assignment of the fundamentals given earlier by Linnett$^5$ and by Herzberg.$^1$ In the present investigation a more general potential function involving all possible force constants has been used. The method adopted for the evaluation of the force constants is the Wilson's F-G matrix method$^6$ making use of symmetry co-ordinates. The latest assignment of frequencies given by Lord and Nolin has been followed. Evaluation of force constants in the case of the deuterium analogue of ethylene oxide has also been made making use of the frequencies given by Lord and Nolin. The molecular parameters have been taken from Cunningham et al.$^7$
Ethylene sulphide molecule possesses the same structure as ethylene oxide. The vibrational spectrum of this molecule has been studied by Thompson and Dupre. The procedure adopted for the evaluation of force constants of ethylene oxide has been extended to the case of ethylene sulphide also.

2. Symmetry Co-ordinates

The internal co-ordinates that are used in the construction of the symmetry co-ordinates are the changes in the bond distances $d_1, d_2, d_3, d_4, D$, $r_1, r_2$ and the changes in the interbond angles $\alpha_1, \alpha_2, \eta_1, \eta_2, \theta, \beta_1, \beta_2, \beta_3, \beta_4, \phi_1, \phi_2, \phi_3, \phi_4$ (Fig. 1).

\[
\begin{align*}
R_1 &= \Delta D \\
R_2 &= (\Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4)/2 \\
R_3 &= (\Delta a_1 + \Delta a_2)/\sqrt{2} \\
R_4 &= (\Delta r_1 + \Delta r_2)/\sqrt{2} \\
R_5 &= \Delta \theta \\
R_6 &= (\Delta d_1 - \Delta d_2 - \Delta d_3 + \Delta d_4)/2 \\
R_7 &= (\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3 + \Delta \beta_4)/2 \\
R_8 &= (\Delta \phi_1 - \Delta \phi_2 - \Delta \phi_3 + \Delta \phi_4)/2 \\
R_9 &= (\Delta r_1 - \Delta r_2)/\sqrt{2} \\
R_{10} &= (\Delta a_1 - \Delta a_2)/\sqrt{2}
\end{align*}
\]

The orthonormalised set of symmetry co-ordinates, satisfying transformation conditions, is constructed as given below:
Potential Constants of Ethylene Oxide

\[ R_{11} = (\Delta \eta_1 - \Delta \eta_2)/\sqrt{2} \]
\[ R_{12} = (\Delta d_1 + d_2 - \Delta d_3 - \Delta d_4)/2 \]

For the \( B_2 \) type,
\[ R_{13} = (\Delta d_1 - \Delta d_2 + \Delta d_3 - \Delta d_4)/2 \]
\[ R_{14} = (\Delta \beta_1 - \Delta \beta_2 + \Delta \beta_3 - \Delta \beta_4)/2 \]
\[ R_{15} = (\Delta \phi_1 - \Delta \phi_2 + \Delta \phi_3 - \Delta \phi_4)/2 \]

3. F Matrix

The general potential function used here involves the force constants \( f_{D}, f_{d}, f_{r}, f_{a}, f_{\beta}, f_{\phi}, f_{\eta}, f_{\theta}, f_{da}, f_{d\alpha}, f_{dr}, f_{d\beta}, f_{d\phi}, f_{da}, f_{d\alpha}, f_{d\beta}, f_{d\phi}, \) and \( f_{\phi}. \) The elements of the potential energy matrix, using the above potential function and the \( U \) and \( U' \) matrices, formed from the coefficients of the internal co-ordinates in the symmetry co-ordinates, are given below for the different vibrational species:

For the \( A_1 \) type:

\[
\begin{bmatrix}
F_{11} & F_{12} & F_{13} & F_{14} & F_{15} \\
F_{21} & F_{22} & F_{23} & F_{24} & F_{25} \\
F_{31} & F_{32} & F_{33} & F_{34} & F_{35} \\
F_{41} & F_{42} & F_{43} & F_{44} & F_{45} \\
F_{51} & F_{52} & F_{53} & F_{54} & F_{55} \\
\end{bmatrix}
= \begin{bmatrix}
f_{D} & 2f_{dd} & 0 & \sqrt{2}f_{dr} & 0 \\
2f_{dd} & f_{d} + f_{dd} & \sqrt{2}df_{da} & \sqrt{2}f_{d\theta} & 0 \\
0 & \sqrt{2}df_{da} & d^2f_{a} & 0 & 0 \\
\sqrt{2}f_{dr} & \sqrt{2}f_{d\theta} & 0 & f_{r} + f_{r\theta} & \sqrt{2}r_{r\theta} \\
0 & 0 & 0 & \sqrt{2}rf_{r\theta} & r^2f_{\theta} \\
\end{bmatrix}
\]

For the \( A_2 \) and \( B_2 \) types the elements are the same:

\[
\begin{bmatrix}
F_{66} & F_{67} & F_{68} \\
F_{76} & F_{77} & F_{78} \\
F_{86} & F_{87} & F_{88} \\
\end{bmatrix} = \begin{bmatrix}
F_{1313} & F_{1314} & F_{1315} \\
F_{1413} & F_{1414} & F_{1415} \\
F_{1513} & F_{1514} & F_{1515} \\
\end{bmatrix} = \begin{bmatrix}
f_{a} - f_{dd} & df_{d\beta} & df_{d\phi} \\
df_{d\beta} & d^2(f_{\beta} - f_{\phi}) & 0 \\
df_{d\phi} & 0 & r^2(f_{\phi} - f_{\phi}) \\
\end{bmatrix}
\]

For the \( B_1 \) type:

\[
\begin{bmatrix}
F_{99} & F_{910} & F_{911} & F_{912} \\
F_{109} & F_{1010} & F_{1011} & F_{1012} \\
F_{119} & F_{1110} & F_{1111} & F_{1112} \\
F_{129} & F_{1210} & F_{1211} & F_{1212} \\
\end{bmatrix} = \begin{bmatrix}
(f_{r} - f_{r\theta}) & 0 & 0 & \sqrt{2}f_{dr} \\
0 & d^2f_{a} & 0 & \sqrt{2}df_{da} \\
0 & 0 & r^2f_{\eta} & 0 \\
\sqrt{2}f_{dr} & \sqrt{2}df_{da} & 0 & (f_{d} + f_{dd}) \\
\end{bmatrix}
\]
4. **G Matrix**

The elements of the kinetic energy matrix corresponding to the different species are obtained following the methods outlined by Wilson and are given below:

For the $A_1$ type:

\[ G_{11} = 2\mu_c \]
\[ G_{22} = \mu_H + \mu_c (1 + \cos \alpha) \]
\[ G_{33} = 2(\mu_H + \mu_c (1 - \cos \alpha))/d^2 \]
\[ G_{44} = \mu_c + \mu_0 (1 + \cos \theta) \]
\[ G_{55} = 2(\mu_c + \mu_0 (1 - \cos \theta))/r^2 \]
\[ G_{12} = 2\mu_c \cos \beta \]
\[ G_{13} = -2\sqrt{2}\mu_c \cos \beta (1 - \cos \alpha)/d \sin \alpha \]
\[ G_{14} = \sqrt{2}\mu_c \cos \eta \]
\[ G_{15} = 2\mu_c \cos \eta (\cos \theta - 1)/r \sin \theta \]
\[ G_{23} = -\sqrt{2}\mu_c \sin \alpha/d \]
\[ G_{24} = \sqrt{2}\mu_c \cos \phi \]
\[ G_{25} = 2\mu_c (\cos \phi \cos \theta + \cos \phi)/r \sin \theta \]
\[ G_{34} = -2\mu_c \cos \phi (1 - \cos \alpha)/d \sin \alpha \]
\[ G_{35} = -2\sqrt{2}\mu_c (1 - \cos \alpha)(\cos \phi \cos \theta + \cos \phi)/rd \sin \alpha \sin \theta \]
\[ G_{45} = -\sqrt{2}\mu_0 \sin \theta/r \]

For the $A_2$ type:

\[ G_{66} = \mu_H + \mu_c (1 - \cos \alpha) \]
\[ G_{77} = \mu_H/d^2 + \mu_c [(1 - \cos \alpha) \{1 + D^2(1/D - \cos \beta/d^2)\} + 2D (1/D - \cos \beta/d) (1 + \cos \alpha)]/D^2 \sin^2 \beta \]
\[ G_{88} = \mu_H/d^2 + \mu_c (1/r - \cos \phi/d)^2 (1 - \cos \alpha)/\sin^2 \phi \]
\[ + \mu_0 \{(1 - \cos \alpha) - (1 + \cos x)/r^2 \sin^2 \phi \}
\[ G_{87} = -\mu_c \{(1/D - \cos \beta/d) (1 - \cos \alpha)/\sin \beta \}
\[ + (1 + \cos x)/D \sin \beta \}
\[ G_{88} = -\mu_c (1/r - \cos \phi/d) (1 - \cos \alpha)/\sin \phi \]
Potential Constants of Ethylene Oxide

\[ G_{78} = \mu_H (\cos \eta - \cos \beta \cos \phi)/d^2 \sin \phi \sin \beta \]
\[ + \mu_c (1/r - \cos \phi/d) [(1/D - \cos \beta/d) (1 - \cos \alpha) \]
\[ + (1 + \cos x)/D]/\sin \phi \sin \beta \]

where \( x = 2\beta - 180 \);

For the B₁ type:

\[ G_{99} = \mu_c + \mu_o (1 - \cos \theta) \]
\[ G_{1010} = 2 \{\mu_H + \mu_c (1 - \cos \alpha)\}/d^2 \]
\[ G_{1111} = \mu_c [(1/D - \cos \eta/r)^2 + (1/r - \cos \eta/D)^2 \]
\[ + 2 \cos \eta (1/D - \cos \eta/r) (1/r - \cos \eta/D) \]
\[ + (1 + 3 \cos^2 \eta)/D^2 + 2/D \{1/D - \cos \eta/r) (\cos^2 \eta + \cos \theta) \]
\[ + 2 \cos \eta (1/r - \cos \eta/D)]/\sin^2 \eta \]
\[ + \mu_o \{(1 - \cos \theta) \cos^2 \eta + 2]/r^2 \sin^2 \eta \]
\[ G_{1212} = \mu_H + \mu_c (1 + \cos \alpha) \]
\[ G_{910} = -2\mu_c \cos \phi (1 - \cos \alpha)/d \sin \alpha \]
\[ G_{911} = -\mu_c \{(1/D - \cos \eta/r) + \cos \eta (1/r - \cos \eta/D) \]
\[ + (\cos^2 \eta + \cos \theta)/D\} + \mu_o \cos \eta (1 - \cos \theta)/r \sin \eta \]
\[ G_{912} = \sqrt{2}\mu_c \cos \phi \]
\[ G_{1011} = 2\mu_c (1 - \cos \alpha) [(1/D - \cos \eta/r) \cos \phi + (1/r - \cos \eta/D) \]
\[ \times \cos \beta + (\cos \beta \cos \eta - \cos \phi)/D]/d \sin \alpha \sin \eta \]
\[ G_{1012} = -\sqrt{2}\mu_c \sin \alpha/d \]
\[ G_{1112} = -\sqrt{2}\mu_c [(1/D - \cos \eta/r) \cos \phi + (1/r - \cos \eta/D) \cos \beta \]
\[ + (\cos \beta \cos \eta - \cos \phi)/D]/\sin \eta \]

For the B₂ type:

\[ G_{1313} = \mu_H + \mu_c (1 - \cos \alpha) \]
\[ G_{1414} = \mu_H/d^2 + \mu_c [(1 - \cos \alpha) \{1 + D^2 (1/D - \cos \beta/d)^2 \}
\[ - 2D (1/D - \cos \beta/d) (1 + \cos x)\}] /D^2 \sin^2 \beta \]
\[ G_{1515} = \mu_H/d^2 + \mu_c (1/r - \cos \phi/d)^2 (1 - \cos \alpha)/\sin^2 \phi \]
\[ + \mu_o \{(1 - \cos \alpha) + (1 + \cos x)\}/r^2 \sin^2 \phi \]
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**TABLE 1**
Potential Constants of Ethylene Oxide

\[ G_{1314} = -\mu_c (1/D - \cos \beta/d) (1 - \cos \alpha)/\sin \beta \]
\[ - (1 + \cos \gamma)/D \sin \beta \]
\[ G_{1315} = -\mu_c (1/r - \cos \phi/d) (1 - \cos \alpha)/\sin \phi \]
\[ G_{1415} = \mu_H (\cos \eta - \cos \beta \cos \phi)/d^2 \sin \phi \sin \beta \]
\[ + \mu_c (1/r - \cos \phi/d) \left[(1/D - \cos \beta/d) (1 - \cos \alpha) \right. \]
\[ - (1 + \cos \gamma)/D \sin \phi \sin \beta. \]

5. RESULTS

Using the elements of the F and G matrices given for the four species of vibrations, the secular equations are obtained for the three molecules in the usual way. These secular equations are then solved for the force constants, by the method of successive approximation. Frequencies are also calculated making use of the set of force constants which forms the best fit. The force constants obtained and the observed and calculated frequencies are presented in Table I.

It is easily seen that the agreement between the observed and calculated frequencies is fairly satisfactory. It may also be noted that the major force constants evaluated for the three molecules are very nearly the same, excepting that in the case of ethylene sulphide, slight changes are observed in the appropriate force constants when the oxygen is replaced by sulphur.

In the case of \( A_2 \) type vibrations in \( \text{C}_2\text{H}_4\text{O} \) the location of the frequency at 1345 cm\(^{-1}\) has been discussed by Lord and Nolin. This frequency is inactive in infra-red and its position in Raman effect is also not definite. In the present investigation, making use of the force constants given for the \( B_2 \) vibrations, this frequency has been found to be 1294 cm\(^{-1}\). In the case of ethylene sulphide this frequency works out to be 938 cm\(^{-1}\).

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