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CALCULATION OF THE VIBRATIONAL FREQUENCIES
OF ETHYLENE

R. W. Goin

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
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CALCULATION OF THE VIBRATIONAL FREQUENCIES
OF ETHYLENE*

By

R. W. Goin

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SUMMARY

Tractable approximations for calculating differential scattering cross sections of molecules for low energy (< 1 ev) neutrons are being sought in this laboratory. These differential cross sections depend on the normal modes of the scattering molecule which are themselves difficult to calculate for large molecules.

In this report, approximations which have been shown to simplify the calculation of the normal modes of paraffin hydrocarbons are tested for olefinic hydrocarbons by application to C_2H_4 , CH_2CD_2 , C_2D_4 . The results indicate that the method should suffice for the low-frequency modes below about 0.1 ev energy, and may be adequate for all vibrations as far as the needs of neutron scattering are concerned.

The normal modes are obtained without and with the approximations for all the molecules considered. These normal modes are valid for calculating the differential cross sections of these molecules in the gas phase.

TABLE OF CONTENTS

	Page
SUMMARY	iii
INTRODUCTION	1
DISCUSSION OF THE PROBLEM	3
COORDINATES	5
1. Axes	5
2. Intragroup Symmetry Coordinates	8
3. Skeletal Symmetry Coordinates	9
KINETIC ENERGY	14
POTENTIAL ENERGY	15
THE SECULAR EQUATION	18
CALCULATIONAL PROCEDURE	20
RESULTS	21
CONCLUSIONS	25
ACKNOWLEDGEMENT	26
LIST OF REFERENCES	27
APPENDIX I	28
APPENDIX II	29
APPENDIX III	31

LIST OF FIGURES

	Page
Figure 1 AXES FOR ETHYLENE	7
Figure 2 INTRAGROUP SYMMETRY COORDINATE DISPLACEMENT PATTERNS	9
Figure 3 SKELETAL SYMMETRY COORDINATE DISPLACEMENT PATTERNS	10
Figure 4 THE A MATRIX FOR ETHYLENE	28
Figure 5 GROUP 1, CH ₂	30
Figure 6 THE D MATRIX FOR ETHYLENE	30
Figure 7 FORCE CONSTANT MATRIX FOR ETHYLENE	31

LIST OF TABLES

Table I	NUMBER OF SKELETAL MODES BELONGING TO EACH REPRESENTATION	10
Table II	EQUILIBRIUM COORDINATES IN EACH CH ₂ GROUP	13
Table III	NORMAL FREQUENCIES OF C ₂ H ₄	22
Table IV	NORMAL FREQUENCIES OF C ₂ D ₄	22
Table V	NORMAL FREQUENCIES OF a - C ₂ H ₂ D ₂	23
Table VI	NORMAL COORDINATES	24

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INTRODUCTION

The calculation of the differential cross section with respect to energy and angle for low energy neutrons requires a knowledge of the vibrational frequencies and the normal modes of the molecule. The practicality of calculating the frequencies and normal modes of complex molecules may depend upon how much simplification can be made without sacrificing accuracy.

McMurry (1)¹ has shown that calculations of the vibrational frequencies of large molecules can be approached by regarding any molecule as an assemblage of atom groups, and choosing the coordinates so that the vibrational modes arise from couplings between "intragroup" vibrations within the groups and "skeletal" vibrations due to rotational and translational motions of the groups. The method is adapted particularly to treating hydrocarbons where the intragroup and skeletal vibrations are often distinct.

McMurry (2) has demonstrated for ethane that the couplings between the intragroup vibrations in the two CH_3 groups can be neglected as can the coupling between the intragroup vibrations on CH_3 and the rotational and translational displacements of the other. Propane has been studied by Marshall (3) using the method of McMurry (1) in which similar conclusions

¹Number in parenthesis refer to references in the List of References.

were drawn; i.e., that the couplings between intragroup vibrations and the rotational and translational displacements can be neglected.

This paper presents similar calculations for ethylene to determine the validity of neglecting the coupling between intragroup and skeletal frequencies in a double bonded hydrocarbon molecule. Frequencies are calculated with all interaction terms included and assuming no interaction between intragroup and skeletal motions, and both sets of calculated frequencies are compared with observed frequencies to determine the effect of neglecting the couplings.

DISCUSSION OF THE PROBLEM

In the section on the secular equation, it is shown how a knowledge of Lagrange's equations of motion provide a basis for calculating the vibrational frequencies of a molecule. In order to obtain the Lagrangian, the kinetic energy and the potential energy must be known. However, the kinetic energy is in terms of cartesian displacements relative to axes fixed in space and the potential energy is usually expressed in terms of changes in interbond angles and bond distances. Thus, in order to solve the Lagrange equations, the potential energy and the kinetic energy must be in the same coordinate system. It should also be noted that it is desirable to choose a coordinate system which does not include those coordinates needed to describe the motion of the center of mass or the overall rotation. A third criterion for choosing the coordinate system is the knowledge that when symmetry exists in the molecule, the coordinate axes should be chosen so that the secular equation factors. This can be seen by looking at Figures 2.a and 2.b. If we call these S_1 and S_2 , respectively, the terms in the potential energy involving these two coordinate axes is of the form

$$PE = k_{11} S_1^2 + k_{22} S_2^2 + k_{12} S_1 S_2 .$$

Now, if a rotation about the Z axis is performed on both displacement patterns, we obtain S_1 and $-S_2$. This would indicate that the potential energy of the molecule depends upon how the coordinate axes are chosen, which is not physically reasonable. Therefore, the cross product term is not allowed. This means that the coordinate should be chosen such that the cross products in the potential energy vanish.

Another consideration in choosing the coordinate system is that the momenta of the molecule must be conserved relative to axes fixed at the

center of mass of the molecule. If there are $3N$ basis vectors (coordinate axes), of which six dictate conservation of momenta, and the $3N$ coordinates form an orthonormal set, then the $3N-6$ basis vectors which describe the internal motions of the molecule will automatically satisfy conservation of momentum of the molecule.

Thus, the problem of calculating the vibrational frequencies of a molecule reduces to choosing a set of coordinate axes which are orthogonal to each other and to the coordinate axes representing linear and angular momentum, determining the transformation from cartesian coordinates to those coordinate axes for the kinetic energy equation, and obtaining a transformation to those coordinate axes from the coordinate axes of the potential energy which involve changes in bond lengths and interbond angles so that the kinetic energy and the potential energy are both in the same basis or coordinate system.

COORDINATES

1. Axes

Each CH_2 or CD_2 group has its own set of axes x, y, z with its origin at the center of mass of the group. These group axes are located with reference to a set of molecular axes X, Y, Z with origin at the center of mass of the entire molecule. Figure 1 shows these axes for ethylene. The equilibrium orientation for the axes x, y, z of both groups is such that they coincide in direction with X, Y, Z , respectively.

Group theory methods (4, chapter 5) tell how to choose coordinate axes which form a basis for a completely reduced representation, and these coordinates when used in the equations of motion separate into sets which do not mix with one another; i.e., their cross product terms do not appear in either the kinetic energy or the potential energy. Hence, the equations of motion involving the members of any one set can be considered by themselves.

A matrix representation of a point group consists in associating with each element, s , of the group a transformation $U(s)$ in such a way that these transformations obey

$$U(s) U(t) = U(st) .$$

If a similarity transformation cannot be found that will reduce the representation (i.e., decrease the number of non-zero off-diagonal elements) it is called an irreducible representation of the group.

If a basis vector $[\alpha_\ell]$ belongs to an irreducible representation, the transformations representing elements of the group may operate on the basis vector with the result that the transformed vector is $\pm [\alpha_\ell]$. In other words, the transformed vector does not have any of the other original basis

vectors as components (unless the representation is degenerate) but is transformed into itself. This also means that the transformation is ± 1 .

The C_2H_4 or C_2D_4 molecule belongs to the D_{2h} point group, and asym- $C_2H_2D_2$ belongs to the C_{2v} point group. This means that the equilibrium configuration of the C_2H_4 molecule is characterized by having symmetry about the X, Y and Z axes, or a threefold symmetry axis; a center of symmetry at the center of mass of the molecule, so that inverting the molecule through that point leaves it in a configuration identical to that before the inversion was made; and three planes of symmetry, the X-Y plane, the Y-Z plane, and the Z-X plane. The asym- $C_2H_2D_2$ molecule is characterized by having one symmetry axis (the Y axis), and two planes of symmetry, X-Y and Y-Z.

The number of normal modes belonging to each irreducible representation of the symmetry point group can be obtained (4, chapter 4) by observing the effect on the displacement pattern of each of the symmetry operations characteristic of the point group. The result for C_2H_4 (and C_2D_4) is that the number of modes belonging to each irreducible representation of the D_{2h} point group are $3A_{1g} + 3B_{1g} + 2B_{2g} + B_{3g} + A_{1u} + 2B_{1u} + 3B_{2u} + 3B_{3u}$. In other words, three modes belong to the A_{1g} irreducible representation of the D_{2h} point group, three belong to the B_{1g} irreducible representation, and so on. The A_{1g} representation is characterized by transforming its basis vectors $[\alpha_\ell]$ by $+1$ for all operations of the point group. B_{1g} transforms by -1 for rotations about Y and Z and reflections in the X-Y plane and the Z-X plane; it has $+1$ for all other operations. B_{2g} has -1 for rotations about X and Y and reflections in the Y-Z plane and the Z-X plane. B_{3g} has -1 for rotations about X and Z and reflections in the X-Y and the

Figure 1
AXES FOR ETHYLENE

Y-Z planes. A_{1u} has -1 for inversion and for reflection in all three planes. B_{1u} has -1 for inversion, rotation about Y and Z, and reflection in the Y-Z plane. B_{2u} has -1 for inversion, rotation about X and Y and reflection in the X-Y plane. B_{3u} has -1 for inversion, rotation about Z and X, and reflection in the Z-X plane. In the above, it is implied that the transformation is +1 for those symmetry operations not mentioned.

Similarly, the normal modes belonging to each irreducible representation of the C_{2v} point group for asym- $C_2H_2D_2$ are $6A_1+2A_2+6B_1+4B_2$. The A_1 representation transforms by +1 for all operations; A_2 transforms by -1 for reflection in the X-Y and the Y-Z planes; B_1 has -1 for rotation about Y and reflection in the X-Y plane; and B_2 has -1 for rotation about Y and reflection in the Y-Z plane.

Symmetry coordinates can be constructed in many ways. In this work as in (1), they will be chosen by (a) using coordinates that are simple combinations of ones which are valid for isolated CH_2 or CD_2 groups, and (b) coordinates which are derived from combinations of rotations and translations of the groups as rigid units. The main advantage of such a choice of coordinates is that the equations of motion can be separated into those involving only displacements within the groups and those involving skeletal displacements. Another advantage is that it is a straightforward way of constructing the symmetry coordinates.

2. Intragroup Symmetry Coordinates

The symmetry of a CH_2 group is that of the C_{2v} point group. An isolated CH_2 group would exhibit three normal non-degenerate modes. Their frequencies could be calculated using three orthogonal symmetry coordinates, two belonging to the A_1 irreducible representation of the C_{2v} point group,

and one belonging to B_2 . Once three symmetry coordinates are obtained for and isolated CH_2 group, symmetry coordinates for C_2H_4 , C_2D_4 , $\text{asym-C}_2\text{H}_2\text{D}_2$ can be obtained from linear combinations of those for each CH_2 or CD_2 group. Figure 2 shows graphically the displacement patterns for each symmetry coordinate and how they are combined linearly to obtain the six intragroup coordinate axes for ethylene. The irreducible representation to which each displacement pattern belongs is also shown in Figure 2.

Figure 2

INTRAGROUP SYMMETRY COORDINATE DISPLACEMENT PATTERNS

3. Skeletal Symmetry Coordinates

The six symmetry coordinates that are made up from intragroup coordinates belong to $2A_{1g} + B_{1g} + B_{2u} + 2B_{3u}$, and the ones corresponding to overall translation and rotation of the molecule belong to $B_{1g} + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$. The skeletal modes, then, belong to $A_{1g} + B_{1g} + B_{2g} + A_{1u} + B_{1u} + B_{2u}$. If skeletal translations are denoted by Q and rotations by Ω , then the symmetry coordinate for skeletal translations is S_Q , and that for rotations is S_Ω . Table I gives the total number of modes belonging to each

representation and indicates whether it is made up of X, Y or Z rotation or translation.

TABLE I

NUMBER OF SKELETAL MODES BELONGING TO EACH REPRESENTATION

	Total Modes	Total Q	Q_X	Q_Y	Q_Z	Total Ω	Ω_X	Ω_Y	Ω_Z
A_{1g}	1	1	0	1	0	0	0	0	0
B_{2g}	1	0	0	0	0	1	0	0	1
B_{3g}	0	0	0	0	0	0	0	0	0
B_{1g}	1	0	0	0	0	1	1	0	0
A_{1u}	1	0	0	0	0	1	0	1	0
B_{2u}	1	0	0	0	0	1	1	0	0
B_{3u}	0	0	0	0	0	0	0	0	0
B_{1u}	1	0	0	0	0	1	0	0	1

The symmetry coordinates corresponding to skeletal displacements can now be determined. The displacement patterns of the skeletal motions are shown in Figure 3.

Figure 3

SKELETAL SYMMETRY COORDINATE DISPLACEMENT PATTERNS

The transformation matrix defining the symmetry coordinates for each group in terms of the mass adjusted cartesian displacements relative to the group axes is

$$S_{\sigma i} = \begin{bmatrix} S_{\alpha i} \\ S_{\beta i} \\ S_{\gamma i} \end{bmatrix} = A_{\sigma i} \sigma_i \quad (1)$$

where $i = 1$ for group 1 and 2 for group 2.

McMurry (1) has demonstrated that the equations for all of the symmetry coordinates, together with those expressing conservation of momenta are conveniently expressed in matrix form as follows:

$$\begin{bmatrix} S_{\sigma} \\ 0 \\ 0 \\ S_{\Omega} \\ 0 \\ 0 \\ S_Q \end{bmatrix} = \begin{bmatrix} A_{\sigma} & 0 & 0 \\ \alpha & 0 & 0 \\ \beta & 0 & 0 \\ 0 & A_{\Omega\Omega} & A_{\Omega Q} \\ 0 & \Delta & \epsilon \\ 0 & 0 & \gamma \\ 0 & 0 & A_Q \end{bmatrix} \cdot \begin{bmatrix} \sigma \\ \Omega \\ Q \end{bmatrix} \quad (2)$$

where σ , Ω , and Q are column matrices of the mass adjusted coordinates and are of the form

$$\sigma = \begin{bmatrix} \sigma_1 \\ \sigma_2 \end{bmatrix}, \text{ and } \sigma_1 = \begin{bmatrix} \sigma_{\alpha 1x} \\ \sigma_{\alpha 1y} \\ \sigma_{\alpha 1z} \\ \sigma_{\beta 1x} \\ \cdot \\ \cdot \\ \cdot \\ \sigma_{\gamma 1z} \end{bmatrix};$$

$$\Omega = \begin{bmatrix} \Omega_1 \\ \Omega_2 \end{bmatrix}, \text{ and } \Omega_1 = \begin{bmatrix} \Omega_{1x} \\ \Omega_{1y} \\ \Omega_{1z} \end{bmatrix}; \quad Q = \begin{bmatrix} Q_1 \\ Q_2 \end{bmatrix}, \text{ and } Q_1 = \begin{bmatrix} Q_{1X} \\ Q_{2Y} \\ Q_{3Z} \end{bmatrix}$$

where $\sigma_{\alpha 1x} = \sqrt{m_{\alpha 1}} \Delta x_{\alpha 1}$; and $\Delta x_{\alpha 1}$ = x component of the displacement of atom α_1

$\dot{\Omega} = \omega_{1x} \sqrt{L_{1x}}$; and ω_{1x} = x component of the angular velocity of group 1

L_{1x} = moment of inertia of group 1 relative to the x axis

$Q_{1x} = \sqrt{M_1} \Delta X_1$; and M_1 = mass of group 1
 ΔX_1 = X component of the displacement of the center of mass of group 1

The α and β matrices are as follows:

$$\alpha = N_1 \begin{bmatrix} \sqrt{m_{\alpha 1}} & 0 & 0 & \sqrt{m_{\beta 1}} & 0 & 0 & \sqrt{m_{\gamma 1}} & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{m_{\alpha 1}} & 0 & 0 & \sqrt{m_{\beta 1}} & 0 & 0 & \sqrt{m_{\gamma 1}} & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{m_{\alpha 1}} & 0 & 0 & \sqrt{m_{\beta 1}} & 0 & 0 & \sqrt{m_{\gamma 1}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{m_{\alpha 2}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{m_{\beta 2}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{m_{\gamma 2}} \end{bmatrix}$$

$$\beta = N_2 \begin{bmatrix} \beta_1 & 0 \\ 0 & \beta_2 \end{bmatrix}$$

$$\beta_1 = \left[\begin{array}{c} \text{where} \\ \sqrt{m_{\alpha 1}} \begin{vmatrix} 0 & z_{\alpha 1} & -y_{\alpha 1} \\ -z_{\alpha 1} & 0 & x_{\alpha 1} \\ y_{\alpha 1} & -x_{\alpha 1} & 0 \end{vmatrix} \sqrt{m_{\beta 1}} \begin{vmatrix} 0 & z_{\beta 1} & -y_{\beta 1} \\ -z_{\beta 1} & 0 & x_{\beta 1} \\ y_{\beta 1} & -x_{\beta 1} & 0 \end{vmatrix} \sqrt{m_{\gamma 1}} \begin{vmatrix} 0 & z_{\gamma 1} & -y_{\gamma 1} \\ -z_{\gamma 1} & 0 & x_{\gamma 1} \\ y_{\gamma 1} & -x_{\gamma 1} & 0 \end{vmatrix} \end{array} \right]$$

$$\beta_2 = \left[\begin{array}{c} \sqrt{m_{\alpha 2}} \begin{vmatrix} 0 & z_{\alpha 2} & -y_{\alpha 2} \\ -z_{\alpha 2} & 0 & x_{\alpha 2} \\ y_{\alpha 2} & -x_{\alpha 2} & 0 \end{vmatrix} \sqrt{m_{\beta 2}} \begin{vmatrix} 0 & z_{\beta 2} & -y_{\beta 2} \\ -z_{\beta 2} & 0 & x_{\beta 2} \\ y_{\beta 2} & -x_{\beta 2} & 0 \end{vmatrix} \sqrt{m_{\gamma 2}} \begin{vmatrix} 0 & z_{\gamma 2} & -y_{\gamma 2} \\ -z_{\gamma 2} & 0 & x_{\gamma 2} \\ y_{\gamma 2} & -x_{\gamma 2} & 0 \end{vmatrix} \end{array} \right]$$

and N_1 and N_2 are such that α and β are normal.

The equilibrium positions for the atoms relative to the x, y, z axes are defined in Table II.

TABLE II
EQUILIBRIUM COORDINATES IN EACH CH₂ GROUP

	α_1	β_1	γ_1	α_2	β_2	γ_2
x^0	0	0	0	0	0	0
y^0	$\frac{-r^0 \cos \theta / 2}{(1+2\kappa_1^2)}$	$\frac{-r^0 \cos \theta / 2}{(1+2\kappa_1^2)}$	$\frac{2\kappa_1^2 r^0 \cos \theta / 2}{(1+2\kappa_1^2)}$	$\frac{r^0 \cos \theta / 2}{(1+2\kappa_2^2)}$	$\frac{r^0 \cos \theta / 2}{(1+2\kappa_2^2)}$	$\frac{-2\kappa_2^2 r^0 \cos \theta / 2}{(1+2\kappa_2^2)}$
z^0	$r^0 \sin \theta / 2$	$-r^0 \sin \theta / 2$	0	$r^0 \sin \theta / 2$	$-r^0 \sin \theta / 2$	0

where θ = equilibrium H-C-H angle, $\kappa_1 = \sqrt{\frac{m_{\alpha 1}}{m_{\gamma 1}}}$, $\kappa_2 = \sqrt{\frac{m_{\alpha 2}}{m_{\gamma 2}}}$

and r^0 = equilibrium C - H distance.

KINETIC ENERGY

When the coordinates are defined as in equation (2), McMurry (1) has shown that the kinetic energy for internal vibration can be written in a simple matrix form

$$2T_v = \begin{bmatrix} \dot{\sigma}' & \dot{\Omega}' & \dot{Q}' \end{bmatrix} \begin{bmatrix} \dot{\sigma} \\ \dot{\Omega} \\ \dot{Q} \end{bmatrix} \quad (3)$$

where the primes denote transposed matrices.

POTENTIAL ENERGY

The potential energy is best expressed in terms of changes in bond lengths and interbond angles. It is convenient to divide them into three types denoted by Σ , χ , and τ having the following definitions:

1. The Σ coordinates are changes in bond distances and interbond angles within the groups. For a CH_2 group, they would be the two C - H distances and the H - C - H angle.
2. The χ coordinates are interbond angles which define the orientation of the groups relative to each other. For a CH_2 group they would be the two H - C - C angles, an angle defining torsional rotation about the C - C line, and an angle defining rocking of the H - C - H plane with respect to the C - C line.
3. The τ coordinates serve to define the geometry of the molecular skeleton. In normal butane, for example, they would include the three C - C distances, the two C - C - C angles, and an angle defining a torsional rotation about the line joining the CH_2 groups. In ethylene, they include only the C - C distance.

These coordinates may be written in matrix form as

$$H = \begin{bmatrix} \Sigma \\ \chi \\ \tau \end{bmatrix} \quad (4)$$

where the Σ coordinates can be associated with specific groups so that

$$\Sigma = \begin{bmatrix} \Sigma_1 \\ \Sigma_2 \end{bmatrix} = \begin{bmatrix} \Delta r_{\alpha 1} \\ \Delta r_{\beta 1} \\ r^0 \Delta \theta_{\alpha \beta 1} \\ \Delta r_{\alpha 2} \\ \Delta r_{\beta 2} \\ r^0 \Delta \theta_{\alpha \beta 2} \end{bmatrix}$$

where r^0 is the equilibrium C - H distance and θ is the H - C - H angle.

The X coordinates are defined as follows:

$$X = \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} r^0 \Delta X_{\alpha 1} \\ r^0 \Delta X_{\beta 1} \\ r^0 \Delta \phi_1 \\ r^0 \Delta \psi_1 \\ r^0 \Delta X_{\alpha 2} \\ r^0 \Delta X_{\beta 2} \\ r^0 \Delta \phi_2 \\ r^0 \Delta \psi_2 \end{bmatrix}$$

where X is the H - C - C angle, ϕ is the angle between the H - C - H plane and the C - C line, and ψ is the torsional rotation about the C - C line.

In ethylene the τ coordinate is just the change in C - C bond distance, ΔR .

In terms of these coordinates in equation (4), the potential energy has the form

$$2V = H' F H \quad (5)$$

where F is the force constant matrix.

The coordinates Σ , X, τ may be expressed in terms of the mass adjusted coordinates σ , Ω , Q by Wilson's method (4, chapter 4). This method is described in Appendix II. This yields the result

$$H = \begin{bmatrix} D_{\Sigma\sigma} & 0 & 0 \\ D_{X\sigma} & D_{X\Omega} & D_{XQ} \\ D_{T\sigma} & D_{T\Omega} & D_{TQ} \end{bmatrix} \begin{bmatrix} \sigma \\ \Omega \\ Q \end{bmatrix} = D A' S \quad (6)$$

where A is given by the matrix relation

$$\begin{bmatrix} S_{\sigma} \\ S_{\Omega} \\ S_Q \end{bmatrix} = \begin{bmatrix} A_{\sigma} & 0 & 0 \\ 0 & A_{\Omega\Omega} & A_{\Omega Q} \\ 0 & 0 & A_{QQ} \end{bmatrix} \begin{bmatrix} \sigma \\ \Omega \\ Q \end{bmatrix} = A \begin{bmatrix} \sigma \\ \Omega \\ Q \end{bmatrix}. \quad (7)$$

Note that to get equation (6) it is necessary that A be orthonormal so that $A^{-1} = A'$.

The potential energy then becomes

$$2V = S' A D' F D A' S. \quad (8)$$

The D matrix for $CX_2 - CY_2$ is given in Appendix II.

THE SECULAR EQUATION

From equations (2) and (3), remembering that $A'A = E$, it is seen that the kinetic energy may be written in terms of the symmetry coordinates as

$$2T_v = \begin{bmatrix} \dot{S}'_\sigma & \dot{S}'_\Omega & \dot{S}'_Q \end{bmatrix} \begin{bmatrix} \dot{S}_\sigma \\ \dot{S}_\Omega \\ \dot{S}_Q \end{bmatrix} = \dot{S}'\dot{S} \quad (9)$$

The Lagrangian is then

$$2L = T - V = \dot{S}'\dot{S} - S'\Gamma S$$

where $\Gamma = A D' F D A'$

The equations of motion are then

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{S}} - \frac{\partial L}{\partial S} = \ddot{S} + \Gamma S = 0 \quad (10)$$

These equations of motion are second order linear differential equations with constant coefficients. Possible solutions are of the form $S_i = A_i \cos(\lambda t + \epsilon)$, where A_i , λ and ϵ are properly chosen constants, and S_i indicates row i of matrix S .

Substituting this solution into (10), the result is

$$-\lambda^2 A \cos(\lambda t + \epsilon) E + \Gamma A \cos(\lambda t + \epsilon) = 0$$

where E is the unit matrix.

Factoring the A_i 's out of each equation, this can be rewritten in matrix form as

$$(\lambda^2 E - A D' F D A') = 0 \quad (11)$$

Only for special values of λ does equation (11) have non-vanishing solutions; these are known as the characteristic values or eigenvalues of the matrix Γ . Equation (11) is the secular equation resulting in the solutions to the equations of motion (equation 10).

It should be pointed out that because the symmetry coordinates belong to irreducible representations of the molecule's point group, Γ is made up of blocks of non-zero elements along the diagonal, the largest in the case of C_2H_4 being 3×3 . Thus, the frequencies associated with each block may be calculated separately and involve relatively low order secular equations.

CALCULATIONAL PROCEDURE

The force constants for ethylene, with one exception, were taken over from Kilpatrick and Pitzer (5), except that their interaction constants k_{H13} and k_{H14} were interchanged and the constant for the A_u torsional oscillation was adjusted. These changes were needed to make the computed frequencies agree with the latest vibrational analysis (6,7). These force constants are given in Appendix III. The H - C - H angles and the C - H and C - C bond distances were taken from Curtis (8). These are $R = 1.350^{\text{\AA}}$, $r = 1.071^{\text{\AA}}$, $\cos\theta/2 = 0.50063$.

The actual matrix multiplications were carried out on the IBM-650 so that to obtain the effect of omitting the coupling between intragroup and skeletal vibrations, the secular equation was solved with

$$A = \begin{bmatrix} A_{\sigma} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \text{ and } A = \begin{bmatrix} 0 & 0 & 0 \\ 0 & A_{\Omega\Omega} & A_{\Omega Q} \\ 0 & 0 & A_{QQ} \end{bmatrix}$$

The secular equation was also solved on the IBM-650 by means of a successive diagonalization technique. This program also obtains the normal coordinates.

RESULTS

The frequencies observed by Crawford, Lancaster and Inskeep⁽⁷⁾, using infrared spectroscopy techniques, for C_2H_4 , C_2D_4 and $CH_2 - CD_2$ are listed in Tables III, IV and V, respectively. The frequencies calculated, making no approximation (A), and assuming no interaction between intragroup and skeletal frequencies (B), are also given in Tables III, IV and V.

The normal coordinates are made up of combinations of the symmetry coordinates. The coefficients of the symmetry coordinates are given for each normal coordinate for C_2H_4 , C_2D_4 and $CH_2 - CD_2$ in Table VI.

TABLE III

NORMAL FREQUENCIES OF C₂H₄

Observed (cm ⁻¹)	Symmetry Species	Calculated			
		A	%Error	B	%Error
3019.3	A _{1g}	3019.9	0	3014.5	- .2
1623.3	A _{1g}	1623.7	0	1495.0	-7.9
1342.4	A _{1g}	1342.9	0	1496.0	11.4
3075.0	B _{1g}	3070.7	-0.1	3070.7	-0.1
1236.0	B _{1g}	1255.2	1.6	1255.2	1.6
3105.5	B _{1g}	3105.5	0	3105.5	0
810.3	B _{2u}	840.0	3.7	840.0	3.7
2989.5	B _{2u}	2989.4	0	2989.4	0
1443.5	B _{3u}	1443.8	0	1443.8	0
943.0	B _{3u}	949.3	0.7	949.3	0.7
1027.0	A _{2g}	1027.0	0	1027.0	0
949.2	B _{1u}	949.1	0	949.1	0

Note: A - no separation of intragroup from skeletal modes

B - intragroup frequencies calculated independently
of skeletal

TABLE IV

NORMAL FREQUENCIES OF C₂D₄

Observed (cm ⁻¹)	Symmetry Species	Calculated			
		A	%Error	B	%Error
2251.0	A _{1g}	2249.9	0	2216.4	- 1.5
1515.0	A _{1g}	1503.0	-0.8	1398.0	- 7.7
981.0	A _{1g}	974.4	-0.7	1181.8	20.8
2304.0	B _{1g}	2311.2	0.3	2311.2	0.3
1006.0	B _{1g}	1017.0	-1.2	1017.9	- 1.2
2345.0	B _{1g}	2317.0	-1.2	2317.0	- 1.2
584.0	B _{2u}	602.7	3.0	602.7	3.0
2200.2	B _{2u}	2160.9	0	2160.9	0
1077.9	B _{3u}	1068.8	-1.7	1068.8	- 1.7
780.0	B _{3u}	780.3	0	780.3	0
726.0	A _{2g}	726.5	0	726.5	0
720.0	B _{1u}	717.9	-0.2	717.9	- 0.2

TABLE V

NORMAL FREQUENCIES OF a - C₂H₂D₂

Observed (cm. ⁻¹)	Symmetry Species	Calculated			
		A	%Error	B	%Error
3019.0	A ₁	3006.3	- 0.4	3002.3	- 0.6
1579.0	A ₁	1596.6	1.1	1447.3	- 8.3
1030.0	A ₁	1056.1	2.5	1472.9	43.0
2228.0	A ₁	2201.5	- 1.2	2188.1	- 1.8
1384.0	A ₁	1335.1	- 3.5	1125.3	18.7
3090.0	B ₁	3088.3	- 0.1	3088.3	- 0.1
660.0	B ₁	502.4	-23.9	502.6	-23.9
2333.0	B ₁	2314.1	- 0.8	2314.1	- 0.8
1150.0	B ₁	1412.4	22.8	1412.8	22.8
889.0	A ₂	937.5	5.5	937.5	5.5
751.3	B ₂	749.8	- 0.2	749.8	- 0.2
943.0	B ₂	949.2	1.0	949.2	1.0

TABLE VI

NORMAL COORDINATES

24

A_{1g}				B_{1g}			B_{2u}			B_{3u}		
	Q_1	Q_2	Q_3		Q_4	Q_5		Q_6	Q_7		Q_8	Q_9
s_1	.8249	.5610	.0694	s_4	1.0000	0	s_6	1.0000	0	s_8	.8369	.5473
s_2	-.4459	.5704	.6898	s_5	0	1.0000	s_7	0	1.0000	s_9	-.5473	.8369
s_3	.3474	-.5999	.7207

2 4

A_{1g}				B_{1g}			B_{2u}			B_{3u}		
	Q_1	Q_2	Q_3		Q_4	Q_5		Q_6	Q_7		Q_8	Q_9
s_1	.7254	.6530	.2179	s_4	1.0000	0	s_6	1.0000	0	s_8	.8079	.5893
s_2	-.4431	.6851	-.5782	s_5	0	1.0000	s_7	0	1.0000	s_9	-.5893	.8079
s_3	-.5268	.3228	.7863

A ₁						B ₁					B ₂		
	Q ₁	Q ₂	Q ₃	Q ₄	Q ₅		Q ₆	Q ₇	Q ₈	Q ₉		Q ₁₀	Q ₁₁
S ₁	.5960	0.5767	.3736	.4114	.0591	S ₆	.7169	.6972	.0005	.0066	S ₁₀	-.6723	.7403
S ₂	.4807	-.145	.3184	.4735	.6558	S ₇	.0046	-.0013	.9052	-.4250	S ₁₁	.7403	.6723
S ₃	.3926	.3528	.4827	.5705	.4038	S ₈	-.6970	.7169	-.0019	-.0139			
S ₄	.5036	.5835	.4241	.4524	.1465	S ₉	-.0138	.0053	.4250	.9051			
S ₅	.0773	.4352	.5885	.2764	.6180								

CONCLUSIONS

From the results of the calculations, it is seen that the frequencies calculated with no coupling between intragroup and skeletal modes are good with the exception of two. These two are the only frequencies which involve a stretching of the C - C bond. This would indicate that not much reliance could be placed on calculated frequencies involving the C - C bond stretching unless the coupling terms for all frequencies involving C - C bond stretching were included. It should be noted that unless the force constants for a particular molecule are fairly well known, errors of the order of 10% could be expected even with all coupling terms included.

The differential cross section with respect to energy and angle for neutrons presently cannot be measured accurately at neutron energies above about 0.2 ev (9). In wave numbers, this is about 800 cm^{-1} . Even the lowest frequency in C_2D_4 , which involves C - C bond stretching, is above this value, so it appears that for the purposes of calculating the differential cross section for low energy neutrons in olefinic hydrocarbons, the coupling between intragroup and skeletal motions can be omitted.

In conclusion, a calculation of the vibrational frequencies of a large hydrocarbon molecule with double bonds in which intragroup and skeletal frequencies were obtained independently would result in fairly good calculated frequencies for modes not involving C - C bond stretching, and even those might be good enough for qualitative frequency assignments and for calculations of neutron scattering.

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APPENDIX I

A Matrix

The complete A matrix has been determined for a general $AX_2 - BY_2$ molecule. The matrix elements are considerably simplified for the C_2H_4 molecule.

The notation used throughout is as follows:

$$K_1^2 = \frac{m\alpha_1}{m_{y_1}}$$

r^0 = equilibrium C - H bond length

R = equilibrium C - C bond length

The irreducible representations of each symmetry coordinate are also listed for both C_2X_4 which belongs to the D_{2h} symmetry point group, and for $CX_2 - CY_2$ which belongs to the C_{2v} symmetry point group.

Figure 4

THE A MATRIX FOR ETHYLENE

APPENDIX II

D Matrix

For a brief example of how the D matrix is obtained, the sub-matrix $D_{\Sigma\sigma}$ will be demonstrated. The other elements of the D matrix are found in a similar manner.

In the $D_{\Sigma\sigma}$ matrix, there is only dependence on the intragroup coordinates; therefore, the $D_{\Sigma\sigma}$ matrix is made up of two sub-matrices, one for each group. These will be the same with the exception of the sign of the y terms. Looking at group 1 as shown in Figure (5), it is seen that a unit vector along the C - H bond going from γ_1 to α_1 is given by

$$\vec{e}_{\alpha_1\gamma_1} = \vec{o}_1 - \frac{\cos\theta/2}{\sqrt{m\alpha_1}} \vec{j} + \frac{\sin\theta/2}{\sqrt{m\alpha_1}} \vec{k}$$

and similarly,

$$\vec{e}_{\beta_1\gamma_1} = \vec{o}_1 - \frac{\cos\theta/2}{\sqrt{m\beta_1}} \vec{j} + \frac{\sin\theta/2}{\sqrt{m\beta_1}} \vec{k}$$

Now, following Wilson (4), the internal coordinates are given by

$$S_t = \sum_{\alpha=1}^N \vec{S}_{t\alpha} \cdot \vec{\rho}_\alpha$$

where α designates which atom is being displaced. The vector $\vec{S}_{t\alpha}$ is explained physically as follows. Let all atoms except atom α be in their equilibrium positions. The direction of $\vec{S}_{t\alpha}$ is the direction in which a given displacement of atoms will produce the greatest increase of S_t . The magnitude $|\vec{S}_{t\alpha}|$ of $\vec{S}_{t\alpha}$ is equal to the increase in S_t produced by a unit displacement of the atom in its most effective direction.

APPENDIX III

F Matrix

The force constant matrix was taken over directly from Kilpatrick and Pitzer (5) because the symmetry coordinates used in their paper correspond directly to those used here. Usually force constants are given in cgs units; however, those given in (5) were converted to atomic mass units and lengths in Angstrom units. This means that the $1/\sqrt{m_{\alpha_i}}$ which was factored out of the D matrix must be in atomic mass units, and the frequencies of vibration in wave numbers, cm^{-1} , are obtained from

$$\tilde{\nu} = 1000 \sqrt{\lambda^2 / m_{\alpha}}$$

where λ^2 are the roots of the secular equation.

The F matrix, together with the numerical values of the force constants are given on the next page.

Δr_{a1}	$\Delta r_{\beta 1}$	$r^{\circ} \theta_1$	Δr_{a2}	$\Delta r_{\beta 2}$	$r^{\circ} \theta_2$	$r^{\circ} X_{a1}$	$r^{\circ} X_{\beta 1}$	$r^{\circ} \phi_1$	$r^{\circ} \psi_1$	$r^{\circ} X_{a2}$	$r^{\circ} X_{\beta 2}$	$r^{\circ} \phi_2$	$r^{\circ} \psi_2$	R	
Δr_{a1}	K_{CH}	k_{H12}	0	k_{H14}	k_{H13}	0									$K_{CH} = 8.580$
$\Delta r_{\beta 1}$	k_{H12}	K_{CH}	0	k_{H13}	k_{H14}	0									$k_{H12} = 0.077$
$r^{\circ} \theta_1$	0	0	H_{β}	0	0	$h_{\beta 12}$									$k_{H13} = -0.053$
Δr_{a2}	k_{H14}	k_{H13}	0	K_{CH}	k_{H12}	0									$k_{H14} = 0.077$
$\Delta r_{\beta 2}$	k_{H13}	k_{H14}	0	k_{H12}	K_{CH}	0									$K_{CC} = 15.667$
$r^{\circ} \theta_2$	0	0	$h_{\beta 12}$	0	0	H_{β}									$H_{\alpha} = 0.8241$
$r^{\circ} X_{a1}$						H_{α}	h_{a12}	0	0	h_{a14}	h_{a13}	0	0	$I_{C\beta}$	$H_{\beta} = 0.5554$
$r^{\circ} X_{\beta 1}$						h_{a12}	H_{α}	0	0	h_{a13}	h_{a14}	0	0	$I_{C\alpha}$	$h_{a12} = 0$
$r^{\circ} \phi_1$						0	0	$F_{\gamma\gamma}$	0	0	0	$f_{\gamma\gamma}$	0		$h_{a13} = -0.0405$
$r^{\circ} \psi_1$						0	0	0	$F_{\phi\infty}$	0	0	0	0		$h_{a14} = 0.0979$
$r^{\circ} X_{a2}$						h_{a14}	h_{a13}	0	0	H_{α}	h_{a12}	0	0	$I_{C\alpha}$	$I_{C\alpha} - I_{C\beta} = 0.4314$
$r^{\circ} X_{\beta 2}$						h_{a13}	h_{a14}	0	0	h_{a12}	H_{α}	0	0	$I_{C\alpha}$	$F_{\phi\infty} = 0.7968$
$r^{\circ} \phi_2$						0	0	$f_{\gamma\gamma}$	0	0	0	$F_{\gamma\gamma}$	0		$F_{\gamma\gamma} = 0.3426$
$r^{\circ} \psi_2$						0	0	0	0	0	0	0	$F_{\phi\infty}$		$f_{\gamma\gamma} = 0.0471$
R	$I_{C\beta}$		$I_{C\beta}$	$I_{C\alpha}$	$I_{C\alpha}$		$I_{C\alpha}$	$I_{C\alpha}$		$I_{C\alpha}$	$I_{C\alpha}$		K_{CC}		$h_{\beta 12} = 0$

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Figure 7

FORCE CONSTANT MATRIX FOR ETHYLENE