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THE CALCULATED NORMAL FREQUENCIES AND
NEUTRON SCATTERING LAW FOR BENZENE

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
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THE CALCULATED NORMAL FREQUENCIES AND NEUTRON SCATTERING LAW FOR BENZENE

BY

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NUCLEAR AND CHEMICAL TECHNOLOGY DIVISION

IDAHO NUCLEAR CORPORATION

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ABSTRACT

Two complete sets of normal modes and frequencies were calculated for a benzene molecule. The first set gives good agreement with the assigned frequencies of Crawford and Miller for the planar vibrations and of Herzberg for the nonplanar vibrations. The second set gives good agreement with the frequency assignments of Shimanouchi.

These normal modes and frequencies were then used to calculate the slow neutron scattering properties of a free gas of benzene molecules. The scattering law, which presents the double differential cross section in terms of the energy and the momentum changes, was calculated for each set of frequencies and modes. The values calculated using the Crawford and Miller-Herzberg assignments are in reasonable agreement with measurements for liquid benzene in those regions of energy and momentum transfer where the intermolecular forces of the liquid state can be neglected. Use of the Shimanouchi frequency assignments gives considerably poorer agreement with the measurements. Therefore, for the other scattering properties only the Crawford and Miller-Herzberg assignments were used.

The calculated values of the total cross section are in good agreement with measured values. Calculated values of the average cosine of the scattering angle and of the diffusion coefficient are somewhat higher than values deduced directly from measured cross sections. A thermal neutron spectrum and pulsed neutron parameters calculated from the scattering law agree fairly well with measurements.

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CHAPTER I

INTRODUCTION

In this paper the fundamental frequencies and normal modes of vibration of a free gas of benzene molecules are calculated and the results used to calculate the neutron scattering law and scattering properties derived from it. The calculated data are compared to measurements reported in the literature and found to be in satisfactory agreement with them. Procedures developed by McMurry and colleagues have been used for calculating both the vibrations and normal modes [1,2] and the scattering law [3,4,5,6].

The scattering law for benzene is of interest because this molecule is the basic structural unit of diphenyl and the terphenyls which are among the most promising organic moderators and coolants for nuclear reactors. In addition, benzene is a somewhat larger molecule, in the sense of having more atoms, than any for which previous calculations have been made by the procedures of McMurry. At the same time, the benzene molecule is not so large as to require modification of existing computer programs for calculating the vibrations and the scattering law, and there are sufficient measurements of the scattering properties of benzene to permit evaluation of the calculated results. Thus, benzene was selected because it permits evaluation of the McMurry procedures for a larger molecule of a different type than those previously considered and because the results for benzene are of some interest in the study of moderators for organic moderated reactors. Extension of the present work to provide scattering laws for diphenyl and the terphenyls appears straightforward but would require extensive computations on a larger computer than was available for calculation of the benzene vibrations.

The calculated scattering law for benzene is in satisfactory agreement with Gläser's measurements on liquid benzene [7,8] in those regions of energy and momentum transfer where intermolecular forces are not important. Over the energy range of 0.006 eV to 0.1 eV the calculated total cross section is in good agreement with the measurements of Rush [9,10]. Values of the diffusion coefficient and average cosine of the scattering angle computed directly from differential cross sections by Hofmeyr [11] are somewhat higher than the values computed from the scattering law of this paper, but the agreement is considered satisfactory. The scattering law of this paper has been used by Griffing [12] for calculations of the thermal neutron parameters in the equation $\lambda = \lambda_0 + DB^2 - CB^4$ and the results are higher than the measured values of Pál et al [13] but λ_0 and C fall within the error limits given. Likewise, Curtis [14] has used the scattering law in the calculation of an infinite medium spectrum of benzene poisoned with boron, and the results are in fair agreement with measured data of Young et al [15]. In summary, the calculated scattering law appears to be satisfactory within the limitations imposed by a free gas model which neglects the intermolecular forces present in liquid benzene, for which all measurements available for comparisons have been made.

At present all procedures for calculating the scattering of neutrons from a molecule which account for the effects of its structure and which provide a quantum mechanical treatment are based on the work of Zemach and Glauber [16]. To the extent that the use of the first Born approximation and the Fermi pseudopotential is justified, their results show that the scattering of a neutron by a molecule is determined by the relative motion of the neutron with respect to the nuclei in the molecule. McMurtry has made it feasible to use the formalism of Zemach and Glauber in calculations by developing approximations which treat rotations of the molecule classically and which treat vibrations classically

when they meet criteria based on the short collision time approximation. For a free gas of molecules, the procedures of McMurry provide a straightforward way of determining the motion of the nuclei, required for calculation of the scattering law, by calculation of the normal frequencies and modes.

The free gas model assumes that there are no intermolecular forces. To find the scattering law for a liquid, McMurry [17] includes frequencies in addition to those arising from the internal vibrations and thus accounts for the intermolecular forces of the liquid state. For this method it is necessary to start with a satisfactory scattering law for the free gas, which the results of this paper provide.

Chapter I is concluded by the following two divisions: (a) a brief review of the literature on the scattering of slow neutrons by molecules and on the calculations of the normal modes and frequencies of molecular vibrations, and (b) a summary of the organization and contents of this paper.

I. Review of the Literature

The effects of chemical binding on the scattering of slow neutrons was first considered by Fermi [18] in 1936 in a paper which gave a theoretical treatment of the scattering cross section of a proton bound to an infinite mass. In this work Fermi used the concepts of the scattering length and the Fermi pseudopotential which are used in most present day calculations of the scattering of slow neutrons from molecules. Sachs and Teller [19] in 1941 were the first to consider the scattering of neutrons from molecular gases. They accounted for the effects of molecular rotation and translation on the total scattering cross section by a mass tensor related to the mass and structure of the molecule by the requirements of conservation of linear and angular momentum. The mass tensor of Sachs and Teller accounts for the dependence of the effective

mass of the molecule on the orientation of the molecule with respect to the direction of the incident neutron and on which nucleus interacts with the neutron.

In 1956 Zemach and Glauber [16] gave the first treatment of scattering of neutrons by molecules that provided a rather exact quantum mechanical description of the process. They derived expressions for the differential cross section that included the effects of all molecular motions and of spin. This work provides the basis for a number of calculations of the scattering of neutrons from molecules, including those of this paper. However, it has usually been found necessary to introduce approximations in addition to those inherent in the use by Zemach and Glauber of the first Born approximation and the Fermi pseudopotential. Krieger and Nelkin [20] developed such an approximation by considering molecular rotation and vibration to be separable and by representing the vibration by the mean-square amplitude of a proton bound in the molecule. Their method has been widely used, and while often satisfactory to provide the scattering data needed for reactor physics calculations, it is usually not able to give good agreement with the scattering law. The approximations formulated by McMurry [3,4,5,6] make it feasible to include all of the internal vibrations of the molecule in the calculation of the scattering law. The interactions of a liquid can be represented approximately by discrete low frequencies.

An alternate approach, in which data from the range where accurate measurements can be made is used to calculate the scattering law over an extended range, was developed by Egelstaff and Schofield [21]. This procedure was incorporated into the LEAP computer program by Macdougall [22].

The expression of the double differential cross section data in the form of the scattering law has been given by Egelstaff [21]. Brugger [23] has discussed an alternate expression in the form of the reduced partial differential cross section.

General reviews of neutron scattering and thermalization have been given by Purohit [24] and Williams [25].

The structure of the benzene molecule, as deduced from spectroscopic data, has been considered by Herzberg [26], and as determined from the molecular orbital approximation of quantum mechanics, by Higasi, Baba, and Rembaum [27].

Wilson, Decius, and Cross [28] have discussed the calculation of the vibrations of a semirigid molecule in great detail. However, their methods require special treatment of redundancies and to the knowledge of the author have not been used as the basis of a computer program. McMurry [1,2] has provided convenient recipes for the calculation of the vibrations of a semirigid molecule which do not require special treatment of redundancies and which are particularly applicable to hydrocarbons, and his methods have been implemented by computer programs. The force constants of the benzene molecule have been determined and fundamental frequencies assigned by Miller and Crawford [29] and by Crawford and Miller [30]. Force constants have also been published by Harada and Shimanouchi [31]. None of these sets of force constants were found to be directly applicable to the present work. Herzberg [26] and Shimanouchi [32] have also selected assignments for the fundamental frequencies.

Gläser [7,8] has measured the scattering law of liquid benzene and has kindly provided the author with the results of his most recent measurements. The total cross section of liquid benzene has been measured by Rush [9,10] and by Antonini and Paoletti [33]. Pál et al [13] have measured the diffusion parameters of liquid benzene by a pulsed neutron technique, and Hofmeyr [11] has calculated the average cosine of the scattering angle and the diffusion coefficient from measurements of the double differential cross section. Boffi, Molinari, and Parks [34] have determined a scattering kernel for benzene that makes rather severe approximations in accounting for the internal vibrations.

II. Content and Organization of Paper

In Chapter II the principal steps are presented for the derivation of the equation for the double differential scattering cross section of a molecule in a definite initial state. The extension to the cross section for molecules in a thermal distribution and the inclusion of spin effects are discussed briefly. Consideration is given to the approximations made in the derivation of the equation for the cross section and to their justification. The way in which the normal modes and frequencies enter into the expression for the cross section is shown. Also, the relation between the scattering cross section and the scattering law is given.

The computation of the normal modes and frequencies of the molecular vibrations is presented in Chapter III. The secular equation as given in matrix form by McMurry [1,2] and the modifications made for the calculations of this paper are presented. The significance of the matrices entering into the secular equations is discussed and the determination of their elements described. A description and a justification of the model assumed for the benzene molecule are given. Assigned frequencies for the normal vibrations are listed and compared with the calculated frequencies.

In Chapter IV the calculated scattering properties of a gas of benzene molecules are presented and compared with measurements reported in the literature. These comparisons are summarized in the first part of Chapter I.

CHAPTER II

THEORY AND ASSUMPTIONS FOR CALCULATION OF THE SCATTERING LAW

The first step in calculating the scattering law for a molecule by the methods used in this paper is the computation of the normal frequencies and modes of the internal vibrations. However, the ways in which the normal frequencies and modes enter into the equations for the scattering law are not immediately obvious. Therefore, the scattering law is considered first and the discussion of the normal frequencies and modes is presented in Chapter III so that their use will be clear when they are discussed.

The derivation of the equations for the scattering law has been carried out in detail by McMurtry [3] and this chapter is essentially a summary of his work. The present discussion shows specifically where the required input data enter into the calculation, makes explicit the assumptions used, and discusses their justification.

The development of this chapter is presented in terms of the double differential scattering cross section. However, the results are presented in Chapter IV in the form of the Egelstaff scattering law and the reduced differential partial cross section. These forms are chosen because they permit a direct comparison with measurements, allow a much more compact presentation of the data,

I. The Relation of the Scattering Law to the Cross Section

The differential cross section is defined so that $\sigma(E_0, E, \theta, \phi)dE d\theta d\phi$ is the number of neutrons scattered per unit time per molecule into unit solid angle about θ and ϕ and emerging with energies in dE about E divided by the incident

flux of neutrons of energy E_0 . Here θ and ϕ are the polar and azimuthal angles, respectively, for spherical coordinates with the polar axis along the direction in which the incident neutrons are traveling; E_0 and E are initial and final energies, respectively, of the neutron. For this work the assumption is made that the benzene gas is an isotropic scatterer and the dependence on ϕ is eliminated. The double differential cross section is then given by

$$\sigma(E_0, E, \mu) = 2\pi\sigma(E_0, E, \theta, \phi) \quad (1)$$

where

$$\mu = \cos \theta \quad (2)$$

The change in notation to μ is conventional and is made because integrations to remove the angular dependence are usually made with $\cos \theta$ as the variable of integration. The double differential cross section specifies both the change in angle and the change in energy, $E - E_0 = \epsilon$, produced by the scattering event. In the derivations it is convenient to designate the double differential cross section by $\sigma(\epsilon, E_0, \mu)$.

The reduced partial differential scattering cross section, $S(\kappa^2, \beta)$, is defined for an isotropic scatterer in terms of the partial differential scattering cross section, $\sigma(E_0, E, \vec{\Omega})$ by the following relation,

$$S(\kappa^2, \beta) = \frac{k_0}{k} e^{\beta/2} \sigma(E_0, E, \theta, \phi) \quad (3)$$

In Equation (3), E_0 and E are the incident and scattered neutron energies, respectively, and $\beta = (E - E_0)/k_B T$, where k_B is the Boltzmann constant in eV/deg and T is the absolute temperature. The k_0 and k are the magnitudes of the incident and scattered neutron wave vectors and $\kappa = \vec{k} - \vec{k}_0$. The Egelstaff scattering law, $S(\alpha, \beta)$ is related to $S(\kappa^2, \beta)$ by the equation.

$$S(\kappa^2, \beta) = \frac{\sigma_b}{4\pi k_B T} S(\alpha, \beta); \quad \alpha = \frac{\kappa^2 \hbar^2}{2MBT} \quad (4)$$

where

σ_b is the bound atom cross section for the principal scatterer hydrogen. As is usual for hydrogenous moderators, the value $M = 1$ atomic unit is used in defining α .

II. The Scattering Cross Section for a Molecule in a Definite Initial State

To find the double differential cross section, the equation which must be solved to some approximation is the Schrödinger equation in the form

$$H_T \Psi(\vec{r}_m, \vec{r}_n) = E \Psi \quad (5)$$

where

H_T is the Hamiltonian operator for the system of the neutron and the molecule,

E is the total energy of the system, which remains constant during the scattering process, and

$\Psi(\vec{r}_m, \vec{r}_n)$ is the wave function of the system. It is a function of the coordinates of the nuclei specified by the single quantity $\vec{r}_m$ and of the neutron specified by $\vec{r}_n$. These coordinates are measured relative to an origin fixed in the laboratory

$$H_T = H_N + H_M + H_I \quad (6)$$

where

H_N is the operator for a free neutron,

H_M is the operator for a free molecule, and

H_I is the interaction between the neutron and the nuclei in the molecule.

$$H_N = \frac{-\hbar^2}{2m_n} \nabla^2(\vec{r}_n) \quad (7)$$

$$H_M = \sum_{\tau} \left[\frac{-\hbar^2}{2m_{\tau}} \nabla^2(\vec{r}_{\tau}) \right] + V(\vec{\rho}_m) \quad (8)$$

$$H_I = \sum_{\tau} V(\vec{r}_n - \vec{r}_{\tau}) \quad (9)$$

where

τ designates the nuclei being considered,

$\vec{\rho}_m$ denotes a set of coordinates relative to axes fixed in the molecule,

m_n is the mass of the neutron, and

m_{τ} is the mass of the τ th nucleus.

The expression of the Hamiltonian for the system as the sum of the three individual Hamiltonians as shown in Equation (6) assumes that the interaction between the neutron and the molecule does not change H_M and H_I during the time of the interaction.

The differential Equation (5) is now converted to an integral equation and the first Born approximation found in a manner similar to that of Schiff [35]. It is assumed that the range of the interaction is short so that the neutron is free in its initial and final states which experimentally determine the scattering cross section. The solution to (5) is approximated by,

$$\psi(\vec{r}_m, \vec{r}_n) = \psi_i(E_i, \vec{r}_m) \frac{e^{i\vec{k}_0 \cdot \vec{r}_n}}{(2\pi)^{3/2}} + v(\vec{r}_m, \vec{r}_n) \quad (10)$$

Here, E_i and E_f are the initial and final energies, respectively, of the molecule. The product $\psi_i \frac{e^{i\vec{k}_0 \cdot \vec{r}_n}}{(2\pi)^{3/2}}$ is the wave function for the plane wave of incident mono-energetic neutrons and a molecule in a definite eigenstate. The term $v(\vec{r}_m, \vec{r}_n)$ will be expressed as a sum of terms each one of which represents the molecule in a definite final state and the neutron as a scattered wave diverging from the region containing the molecule. All of the information about the scattering process

is contained in $v(\vec{r}_m, \vec{r}_n)$. In this treatment the wave equation, Equation (5), and the perturbation $v(\vec{r}_m, \vec{r}_n)$ are written in terms of coordinates fixed in the laboratory. Therefore, the resulting expressions for the cross section are for the laboratory system. This procedure differs from that of Schiff [35] who reduces the wave equation to that for an equivalent one body problem and obtains the cross section in the center of mass system.

Now $v(\vec{r}_m, \vec{r}_n)$ is expressed as the sum of orthonormal wave functions which are solutions to the problem with $H_I = 0$. On using the fact that the total energy of the system is unchanged by the collision and the fact that the point of observation is far from the molecule, the following integral equation is obtained after considerable manipulation and the use of contour integration.

$$v(\vec{r}_m, \vec{r}_n) \approx -(2\pi)^{3/2} \frac{2m_n}{\hbar^2} \frac{e^{ik_f r_n}}{4\pi r_n} \int \psi(E_f, \vec{r}_n) \times \left[\iint \psi_f^*(E_f, \vec{r}_m') H_I \psi(\vec{r}_m', \vec{r}_n') e^{-\vec{k}_f \cdot \vec{r}_n'} dV(\vec{r}_n') dV(\vec{r}_m') \right] dE_f \quad (11)$$

The first Born approximation is found by replacing ψ by

$$\psi \approx \frac{e^{i\vec{k}_o \cdot \vec{r}_n'}}{(2\pi)^{3/2}} \psi_i(E_i, \vec{r}_m') \quad (12)$$

The Fermi pseudopotential [18] is then substituted for H_I to give

$$H_I = - \sum_{\tau} \frac{2\pi}{m_n} a_{\tau} \hbar^2 \delta(\vec{r}_n' - \vec{r}_{\tau}) \quad (13)$$

where

a_{τ} is the bound atom scattering length for the τ^{th} atom.

These substitutions yield

$$v(\vec{r}_m, \vec{r}_n) \approx \int \psi_f(E_f, \vec{r}_m) \frac{e^{i\vec{k}_f \cdot \vec{r}_n}}{r_n} \\ \times \sum_{\tau} \left[a_{\tau} \int \psi_f^*(E_f, \vec{r}'_m) e^{-i\vec{k}_f \cdot \vec{r}'_{\tau}} \psi_i(E_i, \vec{r}'_m) dV(\vec{r}'_m) \right] dE_f \quad (14)$$

where

$$\vec{k}_f = \vec{k}_f - \vec{k}_o$$

The use of the pseudopotential of Fermi [18] is required to justify the use of the first Born approximation. With direct use of the nuclear potential, the first Born approximation can be justified only if the neutrons have energies much greater than 25 MeV [36]. The justification for the use of the Fermi pseudopotential is discussed by Sachs [37]. Briefly, its use is justified by the fact that to the accuracy of the first Born approximation the calculated cross section is the same for any potential that gives the same scattering length. A physical interpretation of this independence of the shape of the potential is that the wavelengths of the slow neutrons being considered are too long to provide information about the shape. Thus, all of the information about the potentials needed for cross section calculations is contained in the scattering lengths for which experimental values are available from cross section measurements. The errors resulting from use of the first Born approximation have been considered by several investigators, and Ringo [38] summarizes the results of these investigations by stating that the error is less than one percent.

Equation (14) gives the wave function from which the cross section for scattering of neutrons by the molecule in state ψ_i is obtained. To get this cross section the emergent neutron wave is represented as the sum of a set of partial waves and the following equation results

$$v_f(E_f, k_f, \vec{r}_n) = \frac{e^{i\vec{k}_f \cdot \vec{r}_n}}{r_n} B(E_f, k_f) \quad (15)$$

where $v(E_f, k_f, \vec{r}_n)$ corresponds to the wave function for scattered neutrons with momentum of magnitude $\hbar k$ and which leave the molecule in an energy between E_f and $E_f + \Delta E_f$. The expansion coefficients are found by multiplying $v(\vec{r}_m, \vec{r})$ by $\psi_f^*(E_f, \vec{r}_m)$, the complex conjugate of ψ_f , and integrating over the molecular coordinates. The result is

$$B(E_f, k_f) = \sum_{\tau} \int \psi_f^*(E_f, \vec{r}_m) a_{\tau} e^{-i\vec{k}_f \cdot \vec{r}_{\tau}} \psi_i(E_i, \vec{r}_m) dV(\vec{r}_m) \quad (16)$$

or in Dirac notation

$$B(E_f, k_f) = \sum_{\tau} \langle \psi_f(E_f, \vec{r}_m) | a_{\tau} e^{-i\vec{k}_f \cdot \vec{r}_{\tau}} | \psi_i(E_i, \vec{r}_m) \rangle \quad (17)$$

The cross section $\sigma_{i,f}(\epsilon_f, E_o, \mu)$ for the scattering angle defined by μ with an energy change $\epsilon_f = \frac{(k_f^2 - k_o^2)\hbar^2}{2m_n}$ is found by inserting $v(E_f, \vec{k}_f, \vec{r}_n)$ into the quantum mechanical expression for the neutron current with the result

$$\sigma_{i,f}(\epsilon_f, E_o, \mu) = 2\pi \frac{k_f}{k_o} B^*(E_f, k_f) B(E_f, k_f) = 2\pi \frac{k_f}{k_o} |B|^2 \quad (18)$$

Inserting $B(E_f, k_f)$ from Equation 17 yields

$$\begin{aligned} \sigma_{i,f} = 2\pi \frac{k_f}{k} \sum_{\tau\tau'} a_{\tau} a_{\tau'} \langle \psi_i(E_i, \vec{r}_m) | e^{i\vec{k}_f \cdot \vec{r}_{\tau}} | \psi_{i'}(E_{i'}, \vec{r}_m) \rangle \\ \times \langle \psi_f(E_f, \vec{r}_m) | e^{-i\vec{k}_f \cdot \vec{r}_{\tau'}} | \psi_i(E_i, \vec{r}_m) \rangle \end{aligned} \quad (19)$$

The dependence of the cross section on the final states is now eliminated.

The following definition is made

$$\sigma_{i,f}(\epsilon, E_0, \mu) \equiv 2\pi \frac{k}{k_0} \sum_{\tau\tau'} a_{\tau} a_{\tau'} \langle \psi_i(E_i, \vec{r}_m) | e^{i\vec{k} \cdot \vec{r}_{\tau}} | \psi_f(E_f, \vec{r}_m) \rangle \times \langle \psi_f(E_f, \vec{r}_m) | e^{-i\vec{k} \cdot \vec{r}_{\tau'}} | \psi_i(E_i, \vec{r}_m) \rangle \quad (20)$$

In this equation k_f has been replaced by an arbitrary k , and the cross section has meaning only when k conforms to the energy difference $E_i - E_f$ between the molecular states ψ_i and ψ_f . The double differential cross section is related to the differential cross section $\sigma_i(E_0, \mu)$ by the equation

$$\sigma_i(E_0, \mu) = \int \left[\int \sigma_{i,f}(\epsilon, E_0, \mu) \delta(E_i - E_f - \epsilon) \right] dE_f \quad (21)$$

The delta function which permits only the $\sigma_{i,f}$ satisfying the requirements on the change of energy to appear, is now expressed by its Fourier representation.

$$\delta(E_i - E_f - \epsilon) = \frac{1}{\hbar} \delta\left(\frac{E_i - E_f - \epsilon}{\hbar}\right) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{\frac{i(E_i - E_f - \epsilon)t'}{\hbar}} dt' \quad (22)$$

For convenience in writing the subsequent equations the following definition is made

$$t \equiv \frac{t'}{\hbar} \quad (23)$$

Then the expression for $\sigma_i(E_0, \mu)$ is

$$\sigma_i(E_0, \mu) = \frac{1}{\hbar} \int \sum_{\tau\tau'} a_{\tau} a_{\tau'} \int \left[\frac{k}{k_0} e^{-i\epsilon t} e^{i(E_i - E_f)t} \times \langle \psi_i | e^{i\vec{k} \cdot \vec{r}_{\tau}} | \psi_f \rangle \langle \psi_f | e^{-i\vec{k} \cdot \vec{r}_{\tau'}} | \psi_i \rangle \right] dt d\epsilon \quad (24)$$

From the relation

$$\sigma_i(E_0, \mu) = \int \sigma_i(\epsilon, E_0, \mu) d\epsilon \quad (25)$$

it follows that

$$\sigma_i(\epsilon, E_o, \mu) = \frac{1}{\hbar} \sum_{\tau\tau'} a_\tau a_{\tau'} \frac{k}{k_o} \int \left[e^{-i\epsilon t} e^{i(E_i - E_f)t} \right. \\ \left. \times \langle \psi_i | e^{i\vec{k} \cdot \vec{r}_\tau} | \psi_f \rangle \langle \psi_f | e^{-i\vec{k} \cdot \vec{r}_{\tau'}} | \psi_i \rangle \right] dt \quad (26)$$

The exponentials $e^{iE_i t}$ and $e^{-iE_f t}$ are now replaced by $e^{iH_M t}$ and $e^{-iH_M t}$ respectively, where H_M is the molecular Hamiltonian operator. In subsequent equations the subscript is dropped and the molecular Hamiltonian is designated by H . The sum over the final states is now made using the closure relation

$$\int \psi_f(E_f, \vec{r}_m) \psi_f^*(E_f, \vec{r}_m') dE_f = \delta(\vec{r}_m - \vec{r}_m') \quad (27)$$

The integration over $\vec{r}_m'$ then gives

$$\sigma_i(\epsilon, E_o, \mu) = \frac{k}{\hbar k_o} \int \left[e^{-i\epsilon t} \right. \\ \left. \times \langle \psi_i(E_i, \vec{r}_m) | \sum_{\tau\tau'} a_\tau a_{\tau'} e^{iHt} e^{i\vec{k} \cdot \vec{r}_\tau} e^{-iHt} e^{-i\vec{k} \cdot \vec{r}_{\tau'}} | \psi_i(E_i, \vec{r}_m) \rangle \right] dt \quad (28)$$

This equation is one of the basic results of Zemach and Glauber[16] and is equation 2.4 of their paper. The objective now is to adapt this equation to semi-rigid molecules in a thermal distribution.

III. The Scattering Cross Section for Molecules in a Thermal Distribution

In order to treat the problem of neutron scattering by a molecule it is necessary to select a rotating coordinate system, separate rotation and vibration, and find the normal coordinates and frequencies for the molecular vibrations. The problem of doing these things has been discussed fully by Wilson[28]. In the present paper the calculation of the normal frequencies and modes is discussed in Chapter III. The purpose in this chapter is to show how they

enter into the calculation of the cross section. For the present work it is assumed that the molecule is rigid enough that rotation-vibration interactions can be neglected, that the vibrations are small enough that the vibrational potential energy can be written as a quadratic form, and that the transformation expressing the normal coordinates in terms of the displacements from their equilibrium positions is known. With these assumptions the molecular Hamiltonian, H , can be written as

$$H \approx H_C + H_R + H_V \quad (29)$$

$$H_V = \sum_{\ell} H_{V\ell} \quad (30)$$

where

H_C is the operator for the translation of the center of mass of the molecule,

H_R is the operator for rotation of the molecule as a whole,

H_V is the operator for the internal vibrations of the molecule.

In terms of normal coordinates

$$H_{V\ell} = \frac{-\hbar^2}{2} \frac{\partial^2}{\partial Q_{\ell}^2} + \frac{1}{2} \lambda_{\ell} Q_{\ell}^2 \quad (31)$$

It is at this point where H_V the operator for the internal vibrations is expressed in terms of the normal coordinates, the Q_{ℓ} 's, that the information from the calculation of the normal modes and frequencies first appears in the scattering problem. In Equation (31), λ_{ℓ} is uniquely determined by the frequency of vibration of the ℓ^{th} mode and Q_{ℓ} can be determined from the calculation of displacements of the nuclei in the ℓ^{th} normal mode.

When Equation (29) is used the operator from Equation (28) can be simplified as follows:

$$e^{iHt} e^{i\vec{k} \cdot \vec{r}_{\tau}} e^{-iHt} e^{-i\vec{k} \cdot \vec{r}_{\tau}} = \hat{0} = \hat{0}_c \hat{0}_{int} \quad (32)$$

where

$$\hat{O}_c = e^{iH_c t} e^{i\vec{k} \cdot \vec{r}_c} e^{-iH_c t} e^{-i\vec{k} \cdot \vec{r}_c} \quad (33)$$

$$\hat{O}_{int} = e^{i(H_R + H_V)t} e^{i\vec{k} \cdot \vec{r}'_\tau} e^{-i(H_R + H_V)t} e^{-i\vec{k} \cdot \vec{r}'_\tau}, \quad (34)$$

and $\vec{r}_c$ is the coordinate for the center of mass of the molecule.

It is now necessary to define the various coordinate systems involved and the relations between them and it is convenient to use matrices for this purpose. The axes fixed in the laboratory system are designated X, Y, Z. There are two sets of axes moving with the center of mass of the molecule. Those designated X', Y', Z' remain parallel to the laboratory system, while those designated x, y, z rotate with the molecule. The vectors $\vec{r}'_\tau$, $\vec{r}_\tau$, are in the system of axes moving with center of mass and must be expressed in terms of the equilibrium positions of the atoms and the normal coordinates.

For this purpose $\vec{r}'_\tau$ and $\vec{r}_\tau$ are represented as column matrices (vectors) whose elements are the components relative to the X', Y', Z' axes which remain parallel to the X, Y, Z axes of the laboratory system. The components of $\vec{r}'_\tau$ or $\vec{r}_\tau$ relative to X', Y', Z' are related to those relative to the rotating axes, x, y, z, by the matrix equation

$$\underline{r}'_\tau = \begin{bmatrix} x'_\tau \\ y'_\tau \\ z'_\tau \end{bmatrix} = \underline{A} \underline{r}_\tau \quad (35)$$

where

$$\underline{r}_\tau = \begin{bmatrix} x_\tau \\ y_\tau \\ z_\tau \end{bmatrix} \quad (36)$$

$$\underline{A} = \begin{bmatrix} \vec{I} \cdot \vec{i} & \vec{I} \cdot \vec{j} & \vec{I} \cdot \vec{k} \\ \vec{J} \cdot \vec{i} & \vec{J} \cdot \vec{j} & \vec{J} \cdot \vec{k} \\ \vec{K} \cdot \vec{i} & \vec{K} \cdot \vec{j} & \vec{K} \cdot \vec{k} \end{bmatrix} \quad (37)$$

A bar under a letter designates a matrix. The matrix of Equation (37) is denoted $\underline{A}$ to conform with general usage; it is not the same as the matrix designated by $\underline{A}$ in Chapter III. In Equation (29) $\vec{I}$, $\vec{J}$, $\vec{K}$ and $\vec{i}$, $\vec{j}$, $\vec{k}$ are unit vectors along X' , Y' , Z' and x , y , z respectively, and the elements $\vec{I} \cdot \vec{i}$, etc., are functions of the Eulerian angles. The use of matrix notation permits writing

$$\vec{\kappa} \cdot \vec{r}'_T \equiv \tilde{\underline{\kappa}} \underline{A} \underline{\rho}_T \quad (38)$$

where $\underline{\kappa}$ is a column matrix with the components of κ along X' , Y' , Z' as elements, and $\tilde{\underline{\kappa}}$ is its transpose.

For these calculations it is necessary to assume that the vibrations are small and with this assumption

$$\underline{\rho}_T = \underline{\rho}_T^0 + \underline{\Delta\rho}_T \quad (39)$$

The transformation to normal coordinates is then of the form

$$\begin{bmatrix} \underline{Q} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \underline{T} \underline{\Delta\rho} = \begin{bmatrix} \underline{T}_Q \\ \underline{T}_{T,R} \end{bmatrix} \underline{\Delta\rho} \quad (40)$$

The problem of finding $\underline{T}$ is discussed in Chapter III and it is through $\underline{T}$ that the calculation of the normal modes enters into the calculation of the scattering law. The following definition is now made

$$\underline{C}_{T\ell} = \underline{A} \underline{T}_{T\ell} \quad (41)$$

where $\underline{T}_{\tau\ell}$ is defined by

$$\underline{T}_{\tau\ell} = \begin{bmatrix} T_{\tau x, \ell} \\ T_{\tau y, \ell} \\ T_{\tau z, \ell} \end{bmatrix} \quad (42)$$

Then the internal operator $\hat{O}_{\text{int}}$ of Equation (34) can be written as

$$\begin{aligned} \hat{O}_{\text{int}} = & e^{iH_R t} e^{\frac{i\tilde{K}A\rho^0}{\tau}} \\ & \times \prod_{\ell} \left(e^{iH_{V\ell} t} e^{\frac{i\tilde{K}C_{\tau\ell}Q_{\ell}}{\tau}} e^{-iH_{V\ell} t} e^{-\frac{i\tilde{K}C_{\tau\ell}Q_{\ell}}{\tau}} \right) \\ & \times e^{-iH_R t} e^{-\frac{i\tilde{K}A\rho^0}{\tau}} \end{aligned} \quad (43)$$

Using Equation (43), the equation for the cross section can be written as

$$\begin{aligned} \sigma_i(\epsilon, E_o, \mu) = & \frac{1}{\hbar} \frac{k}{k_o} \int \left[e^{-i\epsilon t} \langle \psi_{ic} | \hat{O}_c | \psi_{ic} \rangle \right. \\ & \times \sum_{\tau\tau'} a_{\tau} a_{\tau'} \langle \psi_{iR} | e^{iH_R t} e^{\frac{i\tilde{K}A\rho^0}{\tau}} V_{i\tau\tau'} e^{-iH_R t} e^{-\frac{i\tilde{K}A\rho^0}{\tau'}} | \psi_{iR} \rangle \left. \right] dt \end{aligned} \quad (44)$$

where

$$V_{i\tau\tau'} = \prod_{\ell} V_{i\tau\tau', \ell} \quad (45)$$

and

$$\begin{aligned} V_{i\tau\tau', \ell} = & \langle \psi_{i\tau'\ell} | e^{iH_{V\ell} t} e^{\frac{i\tilde{K}C_{\tau\ell}Q_{\ell}}{\tau}} e^{-iH_{V\ell} t} \\ & \times e^{-\frac{i\tilde{K}C_{\tau'\ell}Q_{\ell}}{\tau'}} | \psi_{i\tau\ell} \rangle \end{aligned} \quad (46)$$

Equations (44, 45, 46) give the cross section for scattering by a molecule in a definite eigenstate. This equation reveals all but one item of the data about the molecule and its environment needed to calculate the scattering cross section of a free gas of molecules; the exception is the temperature of the gas.

The data required for the solution of Equation (44) are: (a) The mass of the molecule, which is contained in $\hat{O}_C$, (b) the moments of inertia about principle axes of the molecule which are contained in H_R , (c) the scattering lengths of each of the nuclei, (d) the normal frequencies of the internal vibrations of the molecule, which are contained in $H_{T\ell}$, (e) the transformation matrix T from which the $\underline{C}_{T\ell}$ and the $\underline{Q}_\ell$ matrices can be determined and (f) the $\underline{\rho}_T^0$ matrices. The inclusion of the Maxwellian distribution of states in the actual gas will require that only the moments of inertia be specified rather than the structure of the molecule as implied by the presence of the $\underline{\rho}_T^0$ matrices. However, the structure is required for calculation of both the moment of inertia and the normal modes and frequencies.

To complete the development it remains to (a) account for the Maxwellian distribution of the eigenstates, (b) account for the effects of spin, and (c) introduce the approximations needed to make the calculations feasible.

To obtain the cross section for the Maxwellian distribution of states in the molecular gas, ψ_i is replaced by

$$\psi = \sum_i \alpha_i \psi_i \quad (47)$$

The probability that the interaction will be with a molecule having the energy E_i corresponding to eigenfunction ψ_i is $\alpha_i^* \alpha_i$. The coefficient α_i is written as

$$\alpha_i = \alpha_{pc} \alpha_{qR} \prod_\ell \alpha_{r_\ell} \quad (48)$$

where α_{pc} , α_{qR} , α_{r_ℓ} refer to the center of mass, rotational, and vibrational wave function factors, respectively. Each state ψ_i corresponds to a particular set of indices p, q, r_ℓ so that

$$\psi_i = \psi_{pc} \psi_{qR} \prod_\ell \psi_{r_\ell}^{v_\ell} \quad (49)$$

McMurry [3] shows that the cross section for the gas can be written as $\sigma(\epsilon, E_0, \mu) =$

$$\begin{aligned} \sigma(\epsilon, E_0, \mu) = & \frac{1}{\hbar} \frac{k}{k_0} \int e^{-i\epsilon t} \langle cm \rangle_T \\ & \times \left[\sum_q \sum_{\tau\tau'} |a_{qR}|^2 a_\tau a_{\tau'} \langle \psi_{qR} | e^{iH_R t} e^{i\tilde{k}A_{\rho\tau}^0} \right. \\ & \left. \times \langle \chi_{\tau\tau',v} \rangle_T e^{-iH_R t} e^{-i\tilde{k}A_{\rho\tau}^0} | \psi_{q'R} \rangle \right] dt. \end{aligned} \quad (50)$$

The expressions for the translational expectation $\langle cm \rangle_T$ and for the rotational and vibrational expectation $\langle \chi_{\tau\tau',v} \rangle_T$ have been found by Zemach and Glauber [16] and by McMurry. In the treatment used for the calculation of this paper the rotational and vibrational expectations are separated after the approximation of treating the rotations classically is introduced.

Before introducing approximations the effects of spin must be considered. The scattering lengths a_τ can have two values when the spin of the nucleus is different from zero depending on whether the spins of the nucleus and neutron are parallel or antiparallel. Zemach and Glauber [39] show that when the spins are not coupled to the vibrational and rotational motions a_τ^2 is replaced by $A_\tau^2 + C_\tau^2$ where A_τ and C_τ are the coherent and incoherent scattering amplitudes, respectively. The cross section then contains a sum of terms multiplied by $A_\tau^2 + C_\tau^2$ representing scattering by individual nuclei and a sum of terms multiplied by $A_\tau A_{\tau'}$ ($\tau \neq \tau'$) representing scattering by pairs of atoms, which are neglected in the present treatment. This is the usual assumption for gases or liquids with hydrogen as the principal scatterer. To this approximation the effects of spin are included in the measured values of the scattering lengths $a_\tau^2 = A_\tau^2 + C_\tau^2$. The justification for neglect of interference rests largely on the fact that coherent scattering by hydrogen is weak because of the way the

scattering amplitudes in the singlet and triplet states average. This weakness of the coherent scattering is discussed by Blatt and Weiskopf[40] and by Sachs [37]. The use of this assumption in calculating the scattering law is considered by Goldman[41] and by Purohit [42].

To complete the development the following additional approximations are introduced: (a) rotations are treated classically, (b) averages over orientation replace functions of the Eulerian angle variables by their averages, (c) vibrations with characteristic energies much lower than E_0 are treated classically, and (d) the number of terms in the summations accounting for multiple excitations are limited.

These approximations and their justifications have been considered in considerable detail by McMurry [4] and by McMurry, Gannon, and Hestir [5], and therefore, will be discussed only briefly here. In general the approximations are adequate for a molecular gas over the intermediate ranges of momentum and energy transfers which are of most interest for reactor physics calculations. However, they tend to break down at the lower ranges of interest in determining structural effects and in the higher transition ranges where the nuclei begin to act as though they were not bound to the molecule.

The classical treatment of rotations is based on the fact that molecules with large moments of inertia have densely spaced rotational levels. The classical treatment assumes that angular momenta can be specified exactly, that the molecule is oriented randomly, and that the rotational energies are continuous. It fails when small changes in rotational energy are important.

When the energy of the incident neutron is much higher than the characteristic energy of a normal mode, the vibrations can be treated classically by the same justification as for rotational motion. The computer program used for

the calculations contains criteria to determine whether vibrations should be treated quantum mechanically or classically. If the short collision time approximation is valid it is assumed that the vibrations can be treated classically.

The replacement of the functions of the Eulerian angles by average values is the procedure introduced by Krieger and Nelkin [20]. Griffing [42] has calculated the scattering cross section for methane using a rigorous treatment of the averaging over the orientation, and McMurry, Gannon, and Hestir [5] have compared his results with those using Krieger-Nelkin averaging. Except at forward angles the Krieger-Nelkin averaging gives good results.

The classical treatment of rotation and of some vibrations, the Krieger-Nelkin averaging and the neglect of pair scattering are introduced to make the amount of computer time reasonable. In principal, these assumptions can be removed as larger computers become available. Removal of the restriction to small harmonic vibrations would require further theoretical work and experimental measurements.

CHAPTER III

THE NORMAL FREQUENCIES AND MODES

As discussed in Chapter II, the normal frequencies and modes of the internal vibrations are needed as input data for the calculation of the scattering law. The calculation of the normal frequencies and modes is a straightforward problem in classical mechanics, except for determining the amplitudes of the vibrations. McMurry [1, 2] has developed orderly procedures with convenient recipes for making these calculations and has shown in detail how they are applied. These procedures are especially convenient for molecules because they treat the vibrations in terms of motions by and within the groups comprising the molecules. This method of describing the motions helps in visualizing them and thus in constructing coordinates meeting the symmetry requirements for the atomic displacements. In addition, these procedures avoid the necessity for the special treatment of redundancies in the coordinates. Also, computer programs have been written to make many of the necessary calculations. This chapter considers the application of McMurry's procedures to the benzene molecule but does not attempt a complete development of these procedures.

I. The Secular Equation

McMurry [2] shows that the secular equation which determines the normal frequencies can be written in the form

$$|\lambda \underline{E} - \underline{A} \tilde{\underline{D}} \underline{F} \underline{D} \tilde{\underline{A}}| = 0 \quad (51)$$

The vertical bars designate a determinant; the underlining of a symbol designates a matrix; a tilde designates the transpose of a matrix; and the subscript o specifies a matrix in which the rows have been orthonormalized. In Equation (51) E is a square unit matrix. The other matrices are discussed below.

To obtain the secular equation it is necessary to have expressions for the kinetic and the potential energy. The kinetic energy T is given most directly in terms of mass weighted cartesian displacement coordinates q_i by the equation

$$2T = \sum_{i=1} \dot{q}_i^2 \quad (52)$$

or in matrix form

$$2T = \dot{\underline{q}}^T \dot{\underline{q}} \quad (53)$$

where $\underline{q}$ is a column matrix defined by

$$\underline{q}_m = \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_\tau \\ \vdots \\ q_N \end{bmatrix} ; \quad \underline{q}_\tau = m_\tau^{1/2} \begin{bmatrix} \Delta x_\tau \\ \Delta y_\tau \\ \Delta z_\tau \end{bmatrix} \quad (54)$$

in Equation (54) the Δx_τ etc, are the displacements of atom τ along axes fixed in the molecule, and m_τ is the mass of atom τ .

The potential energy is most directly expressed in valence force coordinates, that is, as changes in bond lengths and interbond angles from their equilibrium values. If $\underline{H}_V$ designates a column matrix with the valence force coordinates as elements, the equation for the potential energy V is

$$2V = \underline{\tilde{H}}_V \underline{F}_V \underline{H}_V \quad (55)$$

Here $\underline{F}_V$ is the matrix giving the force constants for displacements expressed in valence force coordinates. However, in the secular equation T and V must be expressed in the same coordinates. The relation between the two sets of coordinates is given by

$$\underline{H}_V = \underline{D} \underline{q} \quad (56)$$

Wilson et al [28] in Chapter IV give convenient formulas for the $\vec{s}$ vectors which transform from internal coordinates to rectangular coordinates and define the $\underline{D}$ matrix in Appendix VII.

To preserve a relatively simple form for the kinetic energy T the choice is made to transform the potential energy V to the $\underline{q}$ coordinates. The equation for V is then

$$2V = \tilde{\underline{q}} \tilde{\underline{D}} \underline{F}_V \underline{D} \underline{q} . \quad (57)$$

In the literature the force matrices for benzene are usually given for symmetry coordinates because this is the form in which they are most directly related to the spectroscopic and other data from which they are derived. The expression for the potential energy is then

$$2V = \tilde{\underline{H}}_S \underline{F}_S \underline{H}_S . \quad (58)$$

Each row of $\underline{H}_S$ is a valence force symmetry coordinate which is a linear combination of the valence force coordinates that belongs to one of the symmetry species of the molecule's point group. In $\underline{F}_S$ the only nonzero elements are in square blocks about the diagonal of the matrix. Each block corresponds to a symmetry species and has the same number of rows and columns as the number of modes in that species. The matrix $\underline{H}_S$ is related to $\underline{H}_V$ by the matrix equation

$$\underline{H}_S = \underline{U} \underline{H}_V \quad (59)$$

and then

$$\underline{H}_S = \underline{U} \underline{D} \underline{q} = \underline{D}_S \underline{q} ; \underline{D}_S \equiv \underline{U} \underline{D} . \quad (60)$$

The matrix $\underline{U}$ is discussed later in this chapter. Thus, when $\underline{F}_S$ is used the potential energy is given by

$$2V = \tilde{\underline{q}} \tilde{\underline{D}}_S \underline{F}_S \underline{D}_S \underline{q} . \quad (61)$$

However, the secular equation does not factor when the secular equation is written in the mass-weighted coordinates $\underline{q}$. Therefore, symmetry coordinates

$\underline{S}$ which allow the secular equation to be factored are used to express the kinetic and potential energies. The two sets of coordinates are related by

$$\underline{S} = \underline{A}_O \underline{q} \quad (62)$$

For purposes of illustration, assume that $\underline{A}_O$ is square and orthonormal and that all elements in $\underline{S}$ except S_1 are zero. In this case

$$\underline{q} = \tilde{\underline{A}}_O \underline{S} = \tilde{\underline{A}}_O \begin{bmatrix} 0 \\ 0 \\ - \\ - \\ \underline{S}_1 \\ 0 \\ 0 \\ - \end{bmatrix} \quad (63)$$

The displacements in $\underline{q}$ are now proportional to the i th row of $\underline{A}_O$. Each row of $\underline{A}_O$ specifies the displacements of the atoms from equilibrium, that is, a displacement pattern for the molecule. These displacement patterns are chosen so that each one belongs to one of the symmetry species of the molecule's point group. The procedure for finding the rows of $\underline{A}_O$ are discussed in more detail later in this chapter. The kinetic energy T and the potential energy V are now given by

$$2T = \dot{\underline{S}} \dot{\underline{S}} \quad (64)$$

$$2V = \underline{S} \underline{A}_O \underline{\tilde{D}}_S \underline{F}_S \underline{D}_S \underline{\tilde{A}}_O \underline{S} \quad (65)$$

and the secular equation becomes

$$|\lambda \underline{E} - \underline{A}_O \underline{\tilde{D}}_S \underline{F}_S \underline{D}_S \underline{\tilde{A}}_O| = 0 \quad (66)$$

In both Equation (51) and (66) the secular equation is expressed in terms of the symmetry coordinates $\underline{S}$. Wilson et al [28] in Section 6-3 show that when symmetry coordinates are used the secular equation can be factored to the maximum

extent made possible by the symmetry of the molecule. Briefly, the argument goes that the potential energy cannot contain any cross terms $S_i S_j$ between coordinates belonging to different symmetry species. If a symmetry operation left S_i unchanged and changed the sign of S_j the potential energy would be changed, but the potential energy must be invariant to all symmetry operations.

Solution of Equation (66) provides an eigenvalue, λ_τ , for each normal frequency; if some of the modes are degenerate some of the λ_τ 's will have the same value. An eigenvalue is related to the frequency λ_τ of the vibration by the relation

$$\nu_\tau = \frac{\sqrt{\lambda_\tau}}{2\pi} \quad (67)$$

The output data from the computer program [43] which calculates the frequencies is presented in the form of the wave number $\bar{\nu}_\tau$ in units of cm^{-1} which is related to the frequency by the relation

$$\bar{\nu}_\tau = \frac{\nu_\tau}{c} \quad (68)$$

where c is the velocity of light in units of cm per sec. For the calculation of the scattering law, the characteristic energies, E_τ , of the vibrational frequencies are required as input data where

$$E_\tau = h\nu_\tau = hc\bar{\nu}_\tau \quad (69)$$

with Planck's constant h in units of eV-sec.

Previous calculations by McMurry's procedures of the normal modes and frequencies used force matrices expressed in terms of valence force constants [44, 45]. Thus these calculations assumed a secular equation of the form of Equation (51). In the present work it was convenient to use force matrices expressed in terms of valence force symmetry coordinates. Thus it was necessary to transform the secular equation to the form of Equation (66). The transformations were made in a manner which preserved the form of the

secular equation. Since Equations (51) and (66) are of the same form, it was not necessary to modify the computer program used to calculate the normal modes and frequencies.

II. The Model of the Benzene Molecule

The model assumed for the benzene molecule is shown in Figure 1. The carbon atoms lie on the vertices of a hexagon as do the hydrogen atoms and the

Fig. 1 The structural model of a benzene molecule.

molecule has D_{6h} symmetry as designated by Wilson et al [28]. The D_{6h} symmetry requires that the molecule be planar, that all C-C bonds be equivalent, and that all C-H bonds be equivalent. The bond lengths of 1.08 Å for the C-H bonds and 1.39 Å for the C-H bonds are the same as used by Wilson et al [28] and by Crawford and Miller [30].

This D_{6h} model of benzene is now generally accepted, and Herzberg [26] has considered the spectroscopic evidence supporting this model at some length, while Higasi et al [27] show that the molecular orbital approximation of quantum mechanics supports it. Wilson [28], Crawford and Miller [30] and Harada and Schimanouchi [31] have all assumed the D_{6h} model in their work.

For the calculations of the normal frequencies and modes the hydrogen atoms are assumed to be point masses of 1.008 atomic units and the carbon atoms to be point masses of 12.011 atomic units [46].

The coordinate system and the numbering of the atoms used in specifying the elements of the matrices of Equation (66) are also shown in Figure 1.

III. Structure of the Symmetry Representation

To determine the $\underline{A}$ and $\underline{F}_S$ matrices used in the secular equation it is necessary to know the number of normal modes belonging to each symmetry species or irreducible representation. The procedure for finding this structure of the symmetry representation has been completely described by Wilson et al [28] in Chapter VI of their book. In the case of D_{6h} symmetry where all the characters are real, the number of modes belonging to a species, $n(\gamma)$, is found from the equation

$$n(\gamma) = \frac{1}{g} \sum_j g_j \chi_j^{(\gamma)} \chi_j \quad . \quad (70)$$

In Equation (70) g is the number of symmetry operations in the group, 24 for D_{6h} , as shown by Table I of the characters for group D_{6h} . The summation j is over the twelve classes E, C_6 , etc. The number of operations in each class,

TABLE I
CHARACTERS OF THE POINT GROUP D_{6h}

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0

one for E, two for C_6 , etc, is given by g_j . A $\chi_j^{(\gamma)}$ is the character for class j and species $\Gamma^{(\gamma)}$ and is taken directly from Table I, for example, + 1 for class E and species A_{1g} . The χ_j 's are the characters determined by the symmetry operations of the group on the molecule and are determined by contributions from only the unshifted atoms. For example, consider the operation of rotation of 180° about the z axis. Then four atoms are unshifted by the operation and for each of these the x and y coordinates of a displacement are reversed while z is unchanged, so that each unshifted atom contributes -1. Thus the value of χ_j in this example is -4.

The calculation of the number of modes belonging to species A_{1g} is shown in Table II. Continued application of Equation (70) shows that the structure of the symmetry species after removal of modes representing translation or rotation of the molecule as a whole is

$$\Gamma = 2A_{1g} + 2A_{2g} + 4E_{2g} + 2B_{1u} + 2B_{2u} + 3E_{1u} + 2B_{2g} + E_{1g} + A_{2u} + 2E_{2u} \quad (71)$$

Since the dimensionality of the degenerate E modes is two and that all of the other modes is one, there are $3N-6 = 30$ modes as required.

The rows of an A matrix represent displacement patterns in which C-H groups are rotated or translated about the center of mass of the groups or in which the groups move as rigid bodies with respect to the center of mass of the molecule. It is convenient to treat the planar vibrations and the nonplanar vibrations separately. Modes having planar vibrations are identified by having a character for σ_h with a positive value in Table I, while modes having nonplanar vibrations belong to species having characters for σ_h with a negative value. Thus, it is necessary to have the number of modes representing planar translations of the C-H groups, nonplanar translations of the groups, stretching

TABLE II

CALCULATION OF THE NUMBER OF MODES OF A BENZENE MOLECULE BELONGING TO SYMMETRY SPECIES A_{1g}

Operation	g_j	x_j	$x_j^{(\gamma)}$	$g_j x_j x_j^{(\gamma)}$
E	1	1	36	36
C_6	2	1	0	0
C_3	2	1	0	0
C_2	1	1	0	0
C_2'	3	1	-4	-12
C_2''	3	1	0	0
i	1	1	0	0
S_3	2	1	0	0
S_6	2	1	0	0
σ_h	1	1	12	12
σ_d	3	1	0	0
σ_v	3	1	4	12
				48

$$g = 24$$

$$n^{(\gamma)}(A_{1g}) = \frac{1}{24} \times 48 = 2$$

of C-H bonds, etc, belonging to the various species and these are listed in Tables III and IV.

TABLE III
SYMMETRY SPECIES OF THE
PLANAR MODES OF A BENZENE MOLECULE

No.	Species	Type
1	A _{1g}	Group Translation
2	A _{1g}	C-H Bond Stretch
3	A _{2g}	Group Translation
4*	A _{2g}	Molecule Rotation about the X axis
5	E _{2g}	Group Translation
6	E _{2g}	Group Translation
7	E _{2g}	C-H Bond Stretch
8	E _{2g}	Group Rotation
9	E' _{2g}	Group Translation
10	E' _{2g}	Group Translation
11	E' _{2g}	C-H Bond Stretch
12	E' _{2g}	Group Rotation
13	B _{1u}	Group Translation
14	B _{1u}	C-H Bond Stretch
15	B _{2u}	Group Translation
16	B _{2u}	Group Rotation
17	E _{1u}	Group Translation
18	E _{1u}	C-H Bond Stretch
19	E _{1u}	Group Rotation
20*	E _{1u}	Molecule Translation in the Y Direction
21	E' _{1u}	Group Translation
22	E' _{1u}	C-H Bond Stretch
23	E' _{1u}	Group Rotation
24*	E' _{1u}	Molecule Translation in the Z Direction

* Removed for calculation of the normal frequencies and modes

TABLE IV
SYMMETRY SPECIES OF THE
NONPLANAR MODES OF A BENZENE MOLECULE

<u>No.</u>	<u>Species</u>	<u>Type</u>
1	B _{2g}	Group Translation
2	B _{2g}	Group Rotation
3	E _{1g}	Group Translation
4*	E _{1g}	Molecule Rotation about the Z Axis
5	E' _{1g}	Group Translation
6*	E' _{1g}	Molecule Rotation about the Y Axis
7	A _{2u}	Group Rotation
8*	A _{2u}	Molecule Translation in the X Direction
9	E _{2u}	Group Translation
10	E _{2u}	Group Rotation
11	E' _{2u}	Group Translation
12	E' _{2u}	Group Rotation

* Removed for calculation of the normal frequencies and modes

IV. The A Matrices

In the secular equation, Equation (51) or (66), the rows of the matrix A₀ which relates the mass-weighted and symmetry coordinates must be orthonormal. The input data to the computer program does not require that rows be orthonormalized and the corresponding matrix is designated A. The computer program orthogonalizes the rows by the Schmidt process and normalizes them and thus determines A₀ from the matrix A specified by the input data.

Each row of A specifies a displacement pattern of the atoms that must be chosen to belong to one of the symmetry species of the molecules point group. In addition the rows must be linearly independent. These requirements do not

uniquely determine $\underline{A}$, and thus the choice of $\underline{A}$ is somewhat arbitrary. The check for independence must be made only among rows belonging to the same symmetry species since group theory shows that rows belonging to different species must be independent. Within rows belonging to a species this condition is usually apparent from geometrical considerations upon inspection of the displacement patterns. The format for a row of an $\underline{A}$ or a $\underline{D}$ matrix is shown in Table V. The format must be chosen so that the columns of $\underline{A}$ are compatible with the columns of $\underline{D}$, since in the secular equation the products $\underline{A}\tilde{\underline{D}}$ and $\underline{D}\tilde{\underline{A}}$ occur.

TABLE V
FORMAT FOR A ROW OF AN $\underline{A}$ OR A $\underline{D}$ MATRIX

Atom No.	1	2	3	4	5	6	7	8	9	10	11	12
Atom Type	C	H	C	H	C	H	C	H	C	H	C	H
Component	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z	X Y Z
Column	1 2 3	4 5 6	7 8 9	10 11 12	13 14 15	16 17 18	19 20 21	22 23 24	25 26 27	28 29 30	31 32 33	34 35 36

Figures 2 and 3 show the displacement patterns constituting $\underline{A}$. There is no simple mathematical formulation or step by step procedure for determining the rows of $\underline{A}$. For the nondegenerate species they can be found in a relatively straightforward manner by inspection of the symmetry requirements. Consider for example the two patterns belonging to species A_{1g} . The character of the operation σ_h , reflection in the plane of the molecule, is +1 so that all displacements must lie in the plane of the molecule. Operation i , inversion about the center of mass, also has the character +1, so that displacements at opposite vertices of the hexagon must be of equal magnitude but of opposite sign. Consideration of the other operations then quickly reveals the first two patterns of Figure 2. For the degenerate patterns other requirements must be met and the procedure is somewhat more complicated. Then the patterns occur in pairs and in

Fig. 2 The planar symmetry coordinate displacement patterns for a benzene molecule.

Fig. 2 (Contd.) The planar symmetry coordinate displacement patterns for a benzene molecule.

Fig. 2 (Contd.) The planar symmetry coordinate displacement patterns for a benzene molecule.

each member of the pair the effect of a symmetry operation is a linear combination of the effect of the operation on the individual members. In calculating the frequencies and modes two A matrices are selected each containing one member from each pair. To meet the requirements for symmetry coordinates [28] the members within one A matrix must all be the same linear combination of the appropriate pairs.

Fig. 3 The nonplanar symmetry coordinate displacement patterns for a benzene molecule.

V. The U and D Matrices

A matrix U which is used to express the secular equation in the form of Equation (66) is defined by Equation (59) or the equivalent relation

$$\underline{F}_v = \underline{\tilde{U}} \underline{F}_s \underline{U} \quad (72)$$

and the requirement that

$$\underline{\tilde{U}} \underline{U} = 1 \quad (73)$$

The choice of U is not unique and depends on the valence force coordinates used. The U matrix given by Crawford and Miller [30] was used for the calculation of the planar vibrations and that of Miller and Crawford [29] for the nonplanar vibrations.

A computer program written by Boyter and McMurry [47] was used to compute the D matrices for the calculations of the planar and nonplanar vibrations. The valence force coordinates required for the computations of the D matrices were those of Crawford and Miller [30] and Miller and Crawford [29] for the planar and nonplanar cases, respectively, and thus were consistent with the U matrices selected. As previously discussed, Wilson et al [28] have described the procedures for finding the elements of a D matrix. However, it should be noted that Equation 22 in Chapter 4 of Reference 28 is incorrect and should read

$$\vec{s}_{t2} = \frac{r_{23} - r_{12} \cos \phi_2}{r_{23} r_{12} \sin \phi_2} \frac{\vec{e}_{12} \times \vec{e}_{23}}{\sin \phi_2} + \frac{\cos \phi_3}{r_{23} \sin \phi_3} \frac{\vec{e}_{43} \times \vec{e}_{32}}{\sin \phi_3} \quad (74)$$

The format for a row of D is given in Table V. The D_s matrices required as input data for calculations of the vibrations were found by the use of Equation (60).

VI. The Force Matrices

Force matrices which determine the potential energies for displacements in terms of valence force symmetry coordinates have been given by Crawford and Miller [30] for the planar vibrations of benzene and by Miller and Crawford [29] for the nonplanar vibrations. An acceptable force matrix must give satisfactory agreement between the calculated frequencies and those assigned from spectroscopic and other data. The assigned frequencies can be used directly in the scattering calculations, but if the calculated and assigned frequencies are not in satisfactory agreement, the amplitude factors of the normal modes will not be acceptable. For the planar vibrations the assigned frequencies of Crawford and Miller [30] were used as a basis of comparison for the calculated frequencies. For the nonplanar vibrations of Miller and Crawford [29] it was found difficult to correlate the assigned frequencies with the symmetry species, and the assignments given by Herzberg [26] were used. However, there do not appear to be any significant differences between these two assignments for the nonplanar vibrations.

In spite of extensive checking both for numerical errors and for errors in the procedure, it was found using the published force matrices that several of the calculated frequencies differed by large amounts from the assigned frequencies. Repeated attempts to resolve the discrepancies failed and it was found necessary to fit the force matrices to the assigned frequencies. The number of different constants in $\underline{F}_S$ is less than that in $\underline{F}_V$ and with $\underline{F}_S$ it is possible to treat each block independently. Therefore, in fitting the force constants to the assigned frequencies it was convenient to work with Equation (66) which uses $\underline{F}_S$. The fit was made by solving the simultaneous equations

$$\begin{array}{rcl}
\Delta F_1 & = & s_{11}\Delta\nu_1 + s_{12}\Delta\nu_2 + \dots + s_{1n}\Delta\nu_n \\
\vdots & & \vdots \\
\Delta F_n & = & s_{n1}\Delta\nu_1 + s_{n2}\Delta\nu_2 + \dots + s_{nn}\Delta\nu_n
\end{array} \quad (75)$$

In Equation (75) the ΔF 's are the changes to be made in the force constants, the $\Delta\nu$'s are the differences between the assigned and the calculated frequencies, and n is the number of frequencies belonging to the symmetry species. A s_{ij} is the change in frequency ν_j for a unit change in force constant i . These sensitivity coefficients are found by changing one force constant at a time and finding the changes in the calculated frequencies. Equation (75) is strictly true only for very small changes and a number of iterations may be necessary to achieve satisfactory agreement between the calculated and assigned frequencies. There are always more force constants than frequencies except for the case where there is only one frequency belonging to a species, while the maximum number of force constants that can be fitted in any iteration is equal to the number of frequencies. The proper selection of the force constants to be changed is very important in getting rapid convergence to the assigned frequencies. A poor choice can be recognized by the fact that the determinant of the sensitivity coefficients is then very small. In fitting the force constants it was found advantageous in several cases to change the selection of the force constants being altered part way through the iteration process. Also, it was found that changing only the diagonal constants was sometimes quite ineffective. The iterations were continued until the agreement between the assigned and calculated frequencies was better than ± 3 percent. The planar force matrix in symmetry coordinates for the Crawford and Miller [30] assigned frequencies is displayed in Table VI and the nonplanar matrix for the Herzberg [26] assignments in Table VII.

TABLE VI

THE FORCE MATRIX F_s FOR THE
FREQUENCY ASSIGNMENTS OF CRAWFORD AND MILLER
FOR THE PLANAR VIBRATIONS OF A BENZENE MOLECULE

Row	Column of 1st Element	Symmetry Species	Matrix Elements					
1	1	A_{1g}	7.830	-0.420	0	0	0	0
2	1	A_{1g}	-0.420	5.000	0	0	0	0
3	1	A_{2g}	0	0	0.830	0	0	0
4	1	B_{1u}	0	0	0	0.677	0.106	0
5	1	B_{1u}	0	0	0	0.106	5.000	0
6	1	B_{2u}	0	0	0	0	0	5.840
7	7	B_{2u}	0.801	0	0	0	0	0
8	7	E_{2g}	0	0.498	0	0	-0.218	0
9	7	E_{2g}	0	0	5.060	0	0	0
10	7	E_{2g}	0	0	0	4.680	0	0
11	7	E_{2g}	0	-0.218	0	0	1.119	0
12	7	E'_{2g}	0	0	0	0	0	0.498
12	13	E'_{2g}	0	0	-0.218	0	0	0
13	13	E'_{2g}	5.060	0	0	0	0	0
14	13	E'_{2g}	0	4.680	0	0	0	0
15	7	E'_{2g}	0	0	0	0	0	-0.218
15	13	E'_{2g}	0	0	1.119	0	0	0
16	13	E_{1u}	0	0	0	0.822	0	0
17	13	E_{1u}	0	0	0	0	7.600	0
18	13	E_{1u}	0	0	0	0	0	5.140
19	19	E'_{1u}	0.822	0	0	-	-	-
20	19	E'_{1u}	0	7.600	0	-	-	-
21	19	E'_{1u}	0	0	5.140	-	-	-

While these calculations were being made, Shimanouchi[32] published a new set of assigned frequencies for benzene and force matrices were fit to these assignments. The planar force matrix is shown in Table VIII and the non-planar force matrix in Table IX. The calculated and assigned frequencies for

TABLE VII

THE FORCE MATRIX F_s FOR THE
FREQUENCY ASSIGNMENTS OF HERZBERG FOR
THE NONPLANAR VIBRATIONS OF A BENZENE MOLECULE

Row	Column of 1st Element	Symmetry Species	Matrix Elements					
1	1	A _{2u}	0.2461	0	0	0	0	0
2	1	B _{2g}	0	0.1122	-0.0500	0	0	0
3	1	B _{2g}	0	-0.0500	0.5429	0	0	0
4	1	E _{2u}	0	0	0	0.1464	0.0343	0
5	1	E _{2u}	0	0	0	0.0343	0.4020	0
6	1	E' _{2u}	0	0	0	0	0	0.1464
6	7	E' _{2u}	0.0343	0	0	-	-	-
7	1	E' _{2u}	0	0	0	0	0	0.0343
7	7	E' _{2u}	0.0402	0	0	-	-	-
8	7	E _{1g}	0	0.3400	0	-	-	-
9	7	E _{1g}	0	0	0.3400	-	-	-

TABLE VIII

THE FORCE MATRIX F_s FOR THE
FREQUENCY ASSIGNMENTS OF SHIMANOUCI FOR
THE PLANAR VIBRATIONS OF A BENZENE MOLECULE

Row	Column of 1st Element	Symmetry Species	Matrix Elements					
1	1	A _{1g}	7.830	-0.420	0	0	0	0
2	1	A _{1g}	-0.420	5.000	0	0	0	0
3	1	A _{2g}	0	0	0.830	0	0	0
4	1	B _{1u}	0	0	0	0.677	0.106	0
5	1	B _{1u}	0	0	0	0.106	5.000	0
6	1	B _{2u}	0	0	0	0	0	3.752
6	7	B _{2u}	-0.278	0	0	0	0	0
7	1	B _{2u}	0	0	0	0	0	-0.278
7	7	B _{2u}	0.856	0	0	0	0	0
8	7	E _{2g}	0	0.498	0	0	-0.218	0
9	7	E _{2g}	0	0	5.060	0	0	0
10	7	E _{2g}	0	0	0	4.680	0	0

TABLE VIII (Contd.)

THE FORCE MATRIX F_s FOR THE
FREQUENCY ASSIGNMENTS OF SHIMANOUCI FOR
THE PLANAR VIBRATIONS OF A BENZENE MOLECULE

Row	Column of 1st Element	Symmetry Species	Matrix Elements					
11	7	E_{2g}	0	-0.218	0	0	1.119	0
12	7	E'_{2g}	0	0	0	0	0	0.498
13	13	E'_{2g}	5.060	0	0	0	0	0
14	13	E'_{2g}	0	4.680	0	0	0	0
15	7	E'_{2g}	0	0	0	0	0	-0.218
15	13	E'_{2g}	0	0	1.119	0	0	0
16	13	E_{lu}	0	0	0	0.822	0	0
17	13	E_{lu}	0	0	0	0	7.600	0
18	13	E_{lu}	0	0	0	0	0	5.140
19	19	E'_{lu}	0.822	0	0	-	-	-
20	19	E'_{lu}	0	7.600	0	-	-	-
21	19	E'_{lu}	0	0	5.140	-	-	-

TABLE IX

THE FORCE MATRIX F_s FOR THE
FREQUENCY ASSIGNMENTS OF SHIMANOUCI FOR
THE NONPLANAR VIBRATIONS OF A BENZENE MOLECULE

Row	Column of 1st Element	Symmetry Species	Matrix Elements					
1	1	A_{2u}	0.2461	0	0	0	0	0
2	1	B_{2g}	0	0.2104	-0.2697	0	0	0
3	1	B_{2g}	0	-0.2697	0.5429	0	0	0
4	1	E_{2u}	0	0	0	0.1631	0.1478	0
5	1	E_{2u}	0	0	0	0.1478	0.4020	0
6	1	E'_{2u}	0	0	0	0	0	0.1631
6	7	E'_{2u}	0.1478	0	0	-	-	-
7	1	E'_{2u}	0	0	0	0	0	0.1478
7	7	E'_{2u}	0.4020	0	0	-	-	-
8	7	E_{lg}	0	0.3400	0	-	-	-
9	7	E_{lg}	0	0	0.3400	-	-	-

both the Crawford and Miller-Herzberg frequency assignments and the Shimanouchi assignments are given in Table X. The values are in wave numbers with units of cm^{-1} . Also included in Table X are the averages of the squares of the amplitudes of the atomic motion for each of the modes. The amplitudes are all much smaller than the C-C and C-H bond lengths, and thus the criterion for the vibrations to be small, as assumed, is met.

TABLE X

COMPARISON OF ASSIGNED AND CALCULATED
NORMAL FREQUENCIES OF A BENZENE MOLECULE

Planar Vibrations						
Symmetry Species	Crawford and Miller Wave Number (cm ⁻¹)	Calculated (this paper) Wave Number (cm ⁻¹)	Shimanouchi Assignment Wave Number (cm ⁻¹)	Calculated (this paper) Wave Number (cm ⁻¹)	$\langle \Delta r^2 \rangle [a]$ (A ^o) ² x 10 ⁴ [c] (this paper)	
					$\langle \Delta r_H^2 \rangle$	$\langle \Delta r_C^2 \rangle$
A _{1g}	3062	3060	3062	3060	8.0	0.09
A _{1g}	992	996	992	996	3.2	2.1
A _{2g}	1326	1330	1326	1330	16.5	0.4
E _{2g}	3047	3047	3047	3047	16.8 ^[b]	0.1 ^[b]
E _{2g}	1596	1559	1596	1559	18.9 ^[b]	1.4 ^[b]
E _{2g}	1178	1166	1178	1166	21.4 ^[b]	2.1 ^[b]
E _{2g}	606	597	606	597	7.0 ^[b]	7.0 ^[b]
B _{1u}	3060	3058	3068	3058	8.0	0.1
B _{1u}	1010	1015	1010	1015	3.1	2.1
B _{2u}	1648	1644	1310	1306	1.3	1.3
B _{2u}	1110	1112	1150	1147	23.1	0.2
E _{1u}	3080	3075	3063	3075	16.6 ^[b]	0.1 ^[b]
E _{1u}	1485	1482	1486	1482	14.7 ^[b]	1.9 ^[b]
E _{1u}	1037	1031	1038	1031	32.5 ^[b]	1.8 ^[b]
Nonplanar Vibrations						
Symmetry Species	Herzberg Assignment Wave Number (cm ⁻¹)	Calculated (this paper) Wave Number (cm ⁻¹)	Shimanouchi Assignment Wave Number (cm ⁻¹)	Calculated (this paper) Wave Number (cm ⁻¹)	$\langle \Delta r^2 \rangle [a]$ (A ^o) ² x 10 ⁴ [c] (this paper)	
					$\langle \Delta r_H^2 \rangle$	$\langle \Delta r_C^2 \rangle$
B _{2g}	1520	1508	995	993	5.7	1.1
B _{2g}	538	541	703	693	35.4	1.4
E _{1g}	849	851	849	851	51.6 ^[b]	1.1 ^[b]
A _{2u}	671	670	673	670	38.1	0.3
E _{2u}	1160	1160	975	971	20.8 ^[b]	2.3 ^[b]
E _{2u}	404	404	410	420	77.7 ^[b]	5.0 ^[b]
[a] Calculated from Equation (28), Reference 2.						
[b] The $\langle \Delta r_v^2 \rangle$ for the degenerate modes is the sum of the values for the partners.						
[c] Multiply tabulated values by 10 ⁻⁴ .						

CHAPTER IV

THE CALCULATED NEUTRON SCATTERING BY BENZENE AND COMPARISONS WITH MEASUREMENTS

I. The Scattering Law

Figure 4 displays the comparison between the data of Gläser, Ehret and Merkel [7,8] and the calculations for the Egelstaff scattering law, $S(\alpha, \beta)$, as defined by Equation (4). The calculated values are considered to be in satisfactory agreement with measurements when $\beta = 2.0$ or higher and also for the higher α values at lower β 's. However as expected, for the low β 's the values of $S(\alpha, \beta)$ calculated for low α 's are much lower than the data. These departures are attributed to the neglect of intermolecular forces. As in the case of water [17], the inclusion of lower frequencies arising from intermolecular interactions will probably be necessary to improve the agreement between the calculations and measurements. Indeed, preliminary work in this direction supported this view. In Figure 1 it can be seen that for $\beta = 1.5$ or greater the choice of the Crawford and Miller-Herzberg [26,30] frequency assignments gives considerably better agreement with the measurements than if the Shimanouchi [32] assignments are used. Therefore, all subsequent calculations used the Crawford and Miller-Herzberg assignments.

The data in the form of the reduced partial differential cross section $S(\kappa^2, \beta)$, Equation (3), calculated with use of the Crawford and Miller-Herzberg frequency assignments are listed in Table XI. The corresponding data calculated with use of the Shimanouchi frequency assignments are listed in Table XII for values of $\beta = 1.5$ and greater, where the data show a large dependence on the choice of the frequency assignments. The calculations of $S(\kappa^2, \beta)$, the Legendre moments,

Comparisons of Calculated $S(\alpha, \beta)$ per Hydrogen Atom in Benzene with Gläser's Data

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Fig. 4 Comparisons of calculated $S(\alpha, \beta)$ per hydrogen atom in benzene with Gläser's data.

TABLE XI

THE CALCULATED REDUCED PARTIAL CROSS SECTION $S(\kappa^2, \beta)$
 USING THE CRAWFORD AND MILLER-HERZBERG FREQUENCY ASSIGNMENTS

$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **	$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **
7457	1.000	0.000	0.22	1.000	0.400
6044	1.500	0.000	5.60	1.500	0.400
4880	2.250	0.000	45.05	2.250	0.400
3918	3.375	0.000	167.8	3.375	0.400
3120	5.063	0.000	373.4	5.063	0.400
2453	7.594	0.000	585.9	7.594	0.400
1894	11.391	0.000	720.3	11.391	0.400
1422	17.086	0.000	740.1	17.086	0.400
1026	25.629	0.000	658.9	25.629	0.400
697.4	38.443	0.000	515.9	38.443	0.400
436.4	57.665	0.000	354.6	57.665	0.400
244.6	86.498	0.000	211.2	86.498	0.400
120.9	129.75	0.000	108.5	129.75	0.400
57.70	194.62	0.000	53.48	194.62	0.400
27.76	291.93	0.000	26.29	291.93	0.400
518.5	1.000	0.200	--	1.000	0.600
1004	1.500	0.200	0.01	1.500	0.600
1457	2.250	0.200	0.14	2.250	0.600
1738	3.375	0.200	3.62	3.375	0.600
1806	5.063	0.200	28.70	5.063	0.600
1700	7.594	0.200	104.6	7.594	0.600
1480	11.391	0.200	225.1	11.391	0.600
1205	17.086	0.200	336.4	17.086	0.600
916.9	25.629	0.200	385.3	25.629	0.600
646.3	38.443	0.200	357.4	38.443	0.600
414.2	57.665	0.200	275.0	57.665	0.600
235.7	86.498	0.200	176.5	86.498	0.600
117.6	129.75	0.200	99.73	129.75	0.600
56.61	194.62	0.200	48.73	194.62	0.600
27.33	291.93	0.200	24.39	291.93	0.600
--	1.000	0.800	--	1.000	1.500
--	1.500	0.800	--	1.500	1.500
0.01	2.250	0.800	--	2.250	1.500

TABLE XI (Contd.)

THE CALCULATED REDUCED PARTIAL CROSS SECTION $S(\kappa^2, \beta)$
 USING THE CRAWFORD AND MILLER-HERZBERG FREQUENCY ASSIGNMENTS

$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **	$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **
0.03	3.375	0.800	0.19	3.375	1.500
0.80	5.063	0.800	0.95	5.063	1.500
9.60	7.594	0.800	2.88	7.594	1.500
45.44	11.391	0.800	6.24	11.391	1.500
114.6	17.086	0.800	10.91	17.086	1.500
185.4	24.629	0.800	18.41	25.629	1.500
216.6	38.443	0.800	32.77	38.443	1.500
194.4	57.665	0.800	49.92	57.665	1.500
138.0	86.498	0.800	54.59	86.498	1.500
84.97	129.75	0.800	41.65	129.75	1.500
42.94	194.62	0.800	23.70	194.62	1.500
21.97	291.93	0.800	12.51	291.93	1.500
--	1.000	1.000	7.27	1.000	2.000
--	1.500	1.000	9.01	1.500	2.000
--	2.250	1.000	11.04	2.250	2.000
0.01	3.375	1.000	13.39	3.375	2.000
0.03	5.063	1.000	16.08	5.063	2.000
0.45	7.594	1.000	19.15	7.594	2.000
5.98	11.391	1.000	22.62	11.391	2.000
29.77	17.086	1.000	26.25	17.086	2.000
76.05	25.629	1.000	29.44	25.629	2.000
120.84	38.443	1.000	31.69	38.443	2.000
134.04	57.665	1.000	33.67	57.665	2.000
110.33	86.498	1.000	33.90	86.498	2.000
70.00	129.75	1.000	27.21	129.75	2.000
36.73	194.62	1.000	16.01	194.62	2.000
19.27	291.93	1.000	7.51	291.93	2.000
0.86	1.000	2.500			
1.46	1.500	2.500			
2.22	2.250	2.500			
3.16	3.375	2.500			
4.56	5.063	2.500			
7.02	7.594	2.500			

TABLE XI (Contd.)

THE CALCULATED REDUCED PARTIAL CROSS SECTION $S(\kappa^2, \beta)$
USING THE CRAWFORD AND MILLER-HERZBERG FREQUENCY ASSIGNMENTS

$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **
11.10	11.391	2.500
16.69	17.086	2.500
22.73	25.629	2.500
27.32	38.443	2.500
28.62	57.665	2.500
26.19	86.498	2.500
20.09	129.75	2.500
11.60	194.62	2.500
5.43	291.93	2.500
0.38	1.000	3.000
0.56	1.500	3.000
0.94	2.250	3.000
1.73	3.375	3.000
3.10	5.063	3.000
5.07	7.594	3.000
7.53	11.391	3.000
10.42	17.086	3.000
13.98	25.629	3.000
17.96	38.443	3.000
20.70	57.665	3.000
19.99	86.498	3.000
15.39	129.75	3.000
8.83	194.62	3.000
4.32	291.93	3.000

* Barns per molecule per eV per steradian.
** Energy in dimensionless units of $k_B T$.

TABLE XII

THE CALCULATED REDUCED PARTIAL CROSS SECTION $S(\kappa^2, \beta)$
USING THE SHIMANOCHI FREQUENCY ASSIGNMENTS

$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **	$S(\kappa^2, \beta)$ (per molecule)*	κ^2 (Angstroms ⁻²)	β **
--	1.000	1.500	--	1.000	2.500
--	1.500	1.500	--	1.500	2.500
--	2.250	1.500	--	2.250	2.500
0.07	3.375	1.500	0.08	3.375	2.500
0.04	5.063	1.500	0.45	5.063	2.500
1.37	7.594	1.500	1.53	7.594	2.500
3.23	11.391	1.500	3.69	11.391	2.500
6.10	17.086	1.500	6.97	17.086	2.500
11.88	25.629	1.500	10.87	25.629	2.500
25.43	38.443	1.500	14.38	38.443	2.500
43.76	57.665	1.500	16.53	57.665	2.500
51.46	86.498	1.500	17.22	86.498	2.500
41.30	129.75	1.500	15.60	129.75	2.500
24.34	194.62	1.500	10.73	194.62	2.500
12.71	291.93	1.500	5.70	291.93	2.500
4.62	1.000	2.000	0.37	1.000	3.000
5.61	1.500	2.000	0.53	1.500	3.000
6.80	2.250	2.000	0.85	2.250	3.000
8.19	3.375	2.000	1.41	3.375	3.000
9.79	5.063	2.000	2.26	5.063	3.000
11.56	7.594	2.000	3.39	7.594	3.000
13.40	11.391	2.000	4.73	11.391	3.000
15.15	17.086	2.000	6.36	17.086	3.000
16.61	25.629	2.000	8.56	25.629	3.000
18.11	38.443	2.000	11.32	38.443	3.000
21.36	57.665	2.000	13.67	57.665	3.000
25.40	86.498	2.000	14.19	86.498	3.000
23.58	129.75	2.000	12.25	129.75	3.000
15.57	194.62	2.000	8.17	194.62	3.000
7.61	291.93	2.000	4.11	291.93	3.000
* barns per molecule per eV per steradian					
** energy in dimensionless units of $k_B T$					

and the energy moments were made using a computer program written by McMurry and Gannon [48, 49].

II. Legendré Moments and Derived Quantities

The Legendré moments, defined as $\sigma_l(E_0) = \int_0^\infty \int_{-1}^1 \sigma(E_0, E, \mu) P_l(\mu) d\mu dE$,

were calculated for l equal to zero and one and are listed in Table XIII for a set of E_0 in the range 0.00062 $\langle E_0 \rangle$ 1.0 eV. The zeroth moments, $\sigma_0(E_0)$, are the total scattering cross sections. All values for $\sigma_0(E_0)$ and $\sigma_1(E_0)$ include the contributions to the scattering cross section from both hydrogen and carbon even where values are given per hydrogen atom; however, no contributions from absorption are included.

In Figure 5 the calculated values of the total cross section are compared with the measured values of Rush [9,10]. These measured data are consistent with the calculations in including the scattering cross section from carbon, in not including absorption and in being for essentially the same temperature. A number of other measurements of the total cross section of benzene have been made, but usually are either reported with the carbon scattering removed or are ambiguous as to whether or not it has been removed. Antonini and Paoletti [33], who have removed the carbon contribution in their reported values, state that Rush's results are in very good agreement with theirs. Thus, the data of Rush provide a valid basis for comparison of calculations and measurements.

The agreement is good. In fact, the free gas model of benzene gives much better agreement with observed values of the total cross section than the free gas model of water as reported by McMurry et al [17]. Undoubtedly, this is due largely to the fact that the effective mass for scattering by H atoms in benzene;

TABLE XIII

CALCULATED TOTAL CROSS SECTION, AVERAGE COSINE OF THE SCATTERING
ANGLE, AND DIFFUSION COEFFICIENT AS A FUNCTION OF
ENERGY FOR A FREE GAS OF BENZENE MOLECULES AT 295°K

Incident Neutron Energy E_0 (eV)	Total Cross Section		$\sigma_1(E_0)$		$\bar{\mu}(E_0)$	$D(E_0)$ (cm)	$(\overline{\Delta E})_0$	$(\overline{\Delta E})_1$	$(\overline{\overline{\Delta E}})_0$	$(\overline{\overline{\Delta E}})_1$
	Barns per Molecule	Barns per H Atom	Barns per Molecule	Barns per H Atom						
0.00062	884	147.3	8.0	1.3	0.009	0.055	7.51×10^{-3}	-7.54×10^{-2}	2.96×10^{-4}	-1.66×10^{-3}
0.001	749	124.8	8.3	1.4	0.011	0.065	7.60×10^{-3}	-7.25×10^{-2}	3.27×10^{-4}	-1.64×10^{-3}
0.0017	635	105.8	13.9	2.3	0.022	0.078	6.85×10^{-3}	-4.02×10^{-2}	2.61×10^{-4}	-0.94×10^{-3}
0.00225	596	99.4	15.4	2.6	0.026	0.084	6.57×10^{-3}	-3.59×10^{-2}	2.40×10^{-4}	-0.85×10^{-3}
0.003	559	93.2	19.1	3.2	0.034	0.090	6.29×10^{-3}	-2.79×10^{-2}	2.28×10^{-4}	-0.68×10^{-3}
0.0051	507	84.5	28.0	4.7	0.055	0.102	5.72×10^{-3}	-1.61×10^{-2}	2.19×10^{-4}	-0.44×10^{-3}
0.007	482	80.3	31.6	5.3	0.065	0.108	5.57×10^{-3}	-1.32×10^{-2}	2.42×10^{-4}	-0.38×10^{-3}
0.01	451	75.2	37.9	6.3	0.084	0.118	4.93×10^{-3}	-0.90×10^{-2}	2.22×10^{-4}	-0.31×10^{-3}
0.015	420	70.0	43.5	7.3	0.104	0.130	4.29×10^{-3}	-0.54×10^{-2}	2.28×10^{-4}	-0.24×10^{-3}
0.04	317	52.8	62.9	10.5	0.198	0.192	1.48×10^{-3}	0.12×10^{-2}	2.62×10^{-4}	-0.091×10^{-3}
0.05	287	47.8	64.4	10.7	0.224	0.220	0.071×10^{-3}	0.20×10^{-2}	2.84×10^{-4}	-0.079×10^{-3}
0.065	260	43.3	67.7	11.3	0.260	0.255	-2.30×10^{-3}	0.27×10^{-2}	3.99×10^{-4}	-0.051×10^{-3}
0.085	237	39.5	70.7	11.8	0.298	0.295	-6.52×10^{-3}	0.27×10^{-2}	6.39×10^{-4}	-0.022×10^{-3}
0.15	196	32.7	70.2	11.7	0.358	0.388	-26.8×10^{-3}	-0.27×10^{-2}	27.0×10^{-4}	0.27×10^{-3}
0.3	169	28.2	70.6	11.8	0.417	0.498	-80.6×10^{-3}	-3.27×10^{-2}	144×10^{-4}	3.98×10^{-3}
0.65	153	25.5	72.5	12.1	0.473	0.609	-225×10^{-3}	-14.1×10^{-2}	901×10^{-4}	44.4×10^{-3}
1.0	150	25.0	75.4	12.6	0.502	0.657	-382×10^{-3}	-27.3×10^{-2}	2390×10^{-4}	142×10^{-3}

Fig. 5 Comparison of calculated total cross section per hydrogen atom in benzene with Rush's data.

(21.1) is considerably larger than that in free H_2O molecules (1.88). Thus, the recoil effects are less important in benzene. This is supported by the fact that the Nelkin model for water in which $M_H = 18$ gives quite good total cross sections.

The integration errors for $\sigma_0(E)$ and $\sigma_1(E)$ were investigated by determining the effects of finer angular and energy meshes for $E_0 = 0.007$, 0.085, and 1.0 eV. Essentially identical results were obtained with the finer meshes indicating the meshes used for all E_0 were sufficiently fine.

The average cosine of the scattering angle, $\bar{\mu}(E_0)$, and the diffusion coefficient, $D(E_0)$, have been calculated from the relations

$$\bar{\mu}(E_0) = \frac{\sigma_1(E_0)}{\sigma_0(E_0)} \quad (76)$$

and

$$D(E_0) = \frac{1}{3[\Sigma_a(E_0) + \Sigma_o(E_0) - \Sigma_1(E_0)]} \quad (77)$$

The values are listed in Table XIII and compared with values calculated by Hofmeyr [11] from his differential cross section measurements in Figures 6 and 7. While the agreements are reasonably good, the calculated values for $\mu(E_0)$ and $D(E_0)$ lie above those deduced from the scattering. This was also true for water [17]. At the lowest energies, part of the difference for the $D(E_0)$

Fig. 6 Comparison of calculated diffusion coefficient of benzene with Hofmeyr's results.

Fig. 7 Comparison of calculated average cosine of the scattering angle of benzene with Hofmeyr's results.

results arises because the definition of $D(E_0)$ includes absorption. Whereas Hofmeyr defines $D(E_0)$ with including $\Sigma_a(E_0)$; viz,

$$D(E_0) = \frac{1}{3 \Sigma_s(E_0) [1 - \bar{\mu}(E_0)]} \quad (\text{Hofmeyr}) \quad (78)$$

However, most of the differences may result, as for water, because the integration to give μ involves important contributions from regions where α and β are both small. It is in these regions that the model fails.

Also included in Table XIII are values computed for the energy transfer moments, $(\overline{\Delta E})_\ell$ and $(\overline{\Delta E})_\ell$, for $\ell = 1, 2$ defined by

$$(\overline{\Delta E})_\ell = \int_0^\infty \frac{(E - E_0) \sigma_\ell(E_0, E) dE}{\sigma_o(E_0)} \quad (79)$$

$$(\overline{\Delta E})_l = \int_0^{\infty} \frac{(E - E_0)^2 \sigma_l(E_0, E) dE}{\sigma_0(E_0)} \quad (80)$$

Experimental comparisons with these results are not available.

III. The Pulsed Neutron Diffusion Parameters

Pál, Kisdí-Koszó, Bod, Szatmáry, and Vízi [13] used pulsed neutron techniques to measure the thermal neutron diffusion parameters appearing in the equation

$$\lambda = \lambda_0 + DR^2 - CR^4 \quad (81)$$

Table XIV compares their results with those computed from a 33-group kernel calculated from the $S(\alpha, \beta)$ of this paper. These calculations of the diffusion parameters were made by Dr. G. W. Griffing using the TIDE computer program developed at Rensselaer Polytechnic Institute. The calculated parameters are consistently higher than the measured data, but λ_0 and C fall within the given error limits.

TABLE XIV
COMPARISON OF CALCULATED THERMAL DIFFUSION
PARAMETERS OF BENZENE WITH THE MEASUREMENTS OF Pál et al

	$\lambda_0 (\text{sec}^{-1})$	$D (\text{cm}^2/\text{sec})$	$C (\text{cm}^4/\text{sec})$
Calculated	2,973	52,500	17,200
Experiment	$2,886 \pm 111$	$48,649 \pm 1,373$	$13,869 \pm 3,849$

IV. The Thermal Neutron Spectrum

Figure 8 displays the infinite medium neutron spectrum for C_6H_6 poisoned with boron to 5.9 barns per hydrogen atom as computed using a 33-group kernel calculated from the $S(\alpha, \beta)$ of this paper. The comparison is with the data of Young et al [15]. The calculations were made by R. L. Curtis of Idaho Nuclear Corporation using the INCITE program. The agreement is fairly good but improvement is needed at lower energies.

Fig. 8 Comparison of calculated thermal neutron spectrum in benzene poisoned to 5.9 barns per hydrogen atom with Young's data.

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