MOMENTUM transfer to an isolated atom is a simple problem in classical mechanics. However, if the atom which receives the impulse is bound chemically, it is not immediately obvious how the recoil energy becomes distributed among the various internal energy modes of the molecule.

For a diatomic molecule, Suess calculated that the internal energy \( E_i \) will be increased by

\[ \Delta E_i = E_r \left( \frac{\sum m_i m_N}{\sum m_i} \right) \]

where \( m_N \) is the atomic weight of the atom receiving the impulse, \( \sum m_i \) is the molecular weight of the diatomic molecule, and \( E_r \) is the recoil energy acquired by the atom. For gamma-ray recoil, \( E_r = (537 E_{\gamma})/m_N \), where \( E_{\gamma} \) is in units of ev, \( m_N \) in amu, and the gamma-ray energy \( E_{\gamma} \) in Mev.

Steinwedel and Jensen calculated the fractional distribution of the internal energy between the vibrational and rotational modes of a diatomic molecule. In addition, they considered a quantum-mechanical approach to the problem.

Recently, Svoboda discussed the relationship between rotational excitation and the bond dissociation energy. Wolfsberg also included such an effect in his quantum-mechanical evaluation of the beta-decay recoil excitation of \(^{14}C\) labeled ethane.

To calculate the recoil energy required for chemical bond rupture in a polyatomic molecule it is possible to utilize a quantum-mechanical approach. However, because of the uncertainties and assumptions associated with such derivations, the calculated value would be considered as only a very rough approximation.

We have considered the problem of recoil momentum activation of polyatomic molecules in terms of a mechanical model. The model which we propose involves only a small number of well-defined assumptions, and these assumptions, at least for the simpler molecules, may not invalidate the results.

THE MODEL

Consider a molecule as consisting of a group of point masses, the atoms linked together by springs. The molecule, therefore, is not rigid and the atoms in the molecule may undergo independent constrained motions in addition to the translational and rotational motions of the molecule. For a molecule composed of \( N \) atoms, \( 3N \) coordinates will be required to describe the molecule in detail. This can be achieved by first defining a set of coordinates \( r(x, y, z) \) with the center of gravity of the molecule \( G \) as the origin. The coordinates of the center of gravity of the molecule are \( R(X, Y, Z) \) and the translational motion of the center of gravity of the molecule is \( \dot{R} (\dot{X}, \dot{Y}, \dot{Z}) \). The orientation of the molecule in space is usually represented by \( \Theta (\theta, \phi, \chi) \) and thus \( \Theta \) or \( \omega \) is the angular motion of the molecule about its center of gravity.

In addition, the relative positions of the atoms in the molecule can be described as \( r_i (x_i, y_i, z_i) \) (\( i = 1 \) to \( N \)) resulting in \( 3N - 6 \) independent coordinates. Although the positions \( r_i \) describe \( 3N \) coordinates, not all are independent since (1) the choice of the origin as the center of gravity results in

\[ \sum m_i \dot{r}_i = 0 \]

(2)

and (2) the translation and rotation of the molecule has been described by the translation and rotation of the \((x, y, z)\) coordinates, i.e., \( \dot{R} \) and \( \omega \). Thus, there should be no net angular momentum with respect to the \((x, y, z)\) coordinates. As a result.

\[ \sum m_i a_i \times v_i = 0 \]

(3)

where \( a_i \) is the equilibrium position of the \( i \)th atom and \( v_i \) is the vibrational velocity of the \( i \)th atom with respect to the molecule.
When the framework \((X, Y, Z)\) moves at a velocity \(\mathbf{R}\) and rotates at an angular velocity \(\omega\) and the atoms simultaneously vibrate around their equilibrium positions \(\mathbf{a}_i\) at velocities \(\mathbf{v}_i\) then, the space velocity of the \(i\)th atom \(\mathbf{S}_i\) is
\[
\mathbf{S}_i = \mathbf{R} + \omega \times \mathbf{r}_i + \mathbf{v}_i.
\]
Hence, the total energy of the molecule is
\[
E_T = \sum m_i (\mathbf{R} + \omega \times \mathbf{r}_i + \mathbf{v}_i)^2 + V(\mathbf{r}_i). \tag{4}
\]
Since \(\mathbf{r}_i = \omega \times \mathbf{r}_i + \mathbf{v}_i\) and \(\sum m_i \mathbf{r}_i = 0\), it can be shown that
\[
\sum m_i \mathbf{v}_i = 0. \tag{5}
\]
Using Eqs. (2), (3), and (5), the total energy of the system, Eq. (4), is
\[
E_T = \frac{1}{2} \sum m_i \mathbf{R}^2 + \frac{1}{2} \sum m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i)
+ \frac{1}{2} \sum m_i \mathbf{v}_i^2 + \omega \cdot \sum m_i (\mathbf{r}_i \times \mathbf{v}_i) + V(\mathbf{r}_i), \tag{6}
\]
where \(\mathbf{r}_i = \mathbf{r}_i - \mathbf{a}_i\) is the displacement of the \(i\)th atom and \(V(\mathbf{r}_i)\) is the potential energy of the molecule.

The first term on the right-hand side of Eq. (6) is the translational energy of the molecule, the second term is the rotational energy, the third term is the vibrational energy, the fourth term is the rotational and vibrational coupling, and the last term is the potential energy of the molecule.

On the average, \(\mathbf{r}_i\) approaches zero; hence, the internal energy may be approximated by
\[
E_{\text{int}} = \frac{1}{2} \sum m_i (\omega \times \mathbf{a}_i) \cdot (\omega \times \mathbf{a}_i) + \frac{1}{2} \sum m_i \mathbf{v}_i^2 + V(\mathbf{a}_i). \tag{7}
\]

If an atom in the molecule suddenly experiences a mechanical recoil and if the recoil energy is very large compared to the thermal motion of the molecule, then the total energy increase is
\[
\Delta E_T = \frac{1}{2} \sum m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i)
+ \frac{1}{2} \sum m_i \mathbf{v}_i^2 + V(\mathbf{r}_i) - V(\mathbf{a}_i). \tag{8}
\]
The total internal-energy increase is
\[
\Delta E_{\text{int}} = \frac{1}{2} \sum m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) + \frac{1}{2} \sum m_i \mathbf{v}_i^2
+ V(\mathbf{r}_i) - V(\mathbf{a}_i). \tag{9}
\]

### Vibrational and Rotational Energy Separation

Let us now examine the potential-energy change \([V(\mathbf{r}_i) - V(\mathbf{a}_i)]\). This change can result from both the vibrational and rotational motions. The vibrational effect on the potential energy is obvious. The rotational effect on the potential energy can be described as follows. When a molecule is rotating about its center of gravity, centrifugal forces develop stresses in the chemical bonds and, consequently, the bonds are stretched elastically from their original equilibrium positions \(\mathbf{a}_i\) to new equilibrium positions \(\mathbf{b}_i\). This results in a rotational potential-energy change of \([V(\mathbf{b}_i) - V(\mathbf{a}_i)]\). The total potential energy change may be rewritten as
\[
[V(\mathbf{r}_i) - V(\mathbf{b}_i)] + [V(\mathbf{b}_i) - V(\mathbf{a}_i)],
\]
where \([V(\mathbf{r}_i) - V(\mathbf{b}_i)]\) is, therefore, the vibrational potential-energy change. The total internal-energy change \(\Delta E_{\text{int}}\) can be divided into two parts: that resulting from the rotational-energy change \(\Delta E_r\) and that resulting from the vibrational-energy change \(\Delta E_v\), where
\[
\Delta E_{\text{int}} = \frac{1}{2} \sum m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) + V(\mathbf{b}_i) - V(\mathbf{a}_i) \tag{10}
\]
and
\[
\Delta E_v = \frac{1}{2} \sum m_i \mathbf{v}_i^2 + V(\mathbf{b}_i). \tag{11}
\]
Assuming that the atoms vibrate as simple harmonic oscillators around their equilibrium positions \(\mathbf{b}_i\), the vibrational-energy change becomes
\[
\Delta E_v = \frac{1}{2} \sum m_i \mathbf{v}_i^2, \tag{12}
\]
where \(\mathbf{v}_i\) is the vibrational velocity of the \(i\)th atom at its equilibrium location \(\mathbf{b}_i\).

### Momentum Excitation in Each Bond

Equations (10) and (12) represent the total vibrational- and rotational-energy changes due to an impulse \(Q\) received by an atom \(N\). Although this sudden impulse \(Q\) will excite principally those bonds which link atom \(N\) to the remainder of the molecule; it will also cause some excitation in the other bonds in the molecule. In order to be able to calculate the impulse required to rupture a particular bond, it is necessary to express \(\Delta E_r\) and \(\Delta E_v\) as sums of the energy changes in each bond. The resulting expressions will depend upon the molecular configurations.

Let us consider a molecule which consists of a center atom \(\mathbf{C}\) and \((i-1)\) remaining atoms \([1, 2, \ldots, j, \ldots, (i-1)]\) which are joined only to atom \(\mathbf{C}\). (Typical examples of such compounds are: \(\text{CH}_3\text{Br}\), where the Br receives the impulse; \(\text{PCI}_3\), where the Cl receives the impulse; \(\text{CH}_3\text{CH}_2\text{Br}\), where the Br receives the impulse, and the \(\text{CH}_3\) is considered as a point mass. If the carbon in a compound such as \(\text{CH}_3\text{Br}\) receives the impulse, a slight modification of the final result is needed.) We define the bond which connects atoms \(\mathbf{C}\) and \(j\) as \(\mathbf{f}\), and we define the vibrational and rotational-induced energy changes associated with this bond as \(\Delta E_{v\mathbf{f}}\) and \(\Delta E_{r\mathbf{f}}\), respectively.
MOMENTUM TRANSFER TO AN ATOM IN A MOLECULE

Vibrational-Energy Contribution

Using Eqs. (5) and (12), the vibrational-energy contribution is found to be

$$\Delta E_v = \sum_{j=1}^{N-1} \Delta E_{ij} = \frac{1}{2} \sum_{j=1}^{N-1} m_j \omega_j^2 (v_{ij} - v_{ij0}) \cdot (v_{ij} - v_{ij0}).$$  \hspace{1cm} (13)

Hence, the vibrational-energy change in bond $j$ is

$$\Delta E_{ij} = \frac{1}{2} m_j \omega_j^2 (v_{ij} - v_{ij0}).$$  \hspace{1cm} (14)

Rotational-Energy Contribution

The rotational-energy change is separated on the basis that the rotational excitation of the chemical bonds is due to the centrifugal stresses developed in the bonds.

The centrifugal forces associated with atoms $j$ and $C$ are $F_j = m_j \omega_j^2 r_j$ and $F_C = m_C \omega_j^2 r_C$; however, $F_C = - \sum_j F_j$. Hence, the centrifugal force can be resolved into $-F_j$ components ($j = 1$ to $j = i-1$). The stress in bond $j$ will be due to the centrifugal force $F_j$ on the $j$th atom and a portion of the centrifugal force of the atom $C$, $-F_j$. Depicted in Fig. 1 are the forces acting on the bond $j$, where $G$ is the center of gravity and $\alpha_j$ is the angle between $Gj$ and $Cj$.

The vector $F_j$ is next resolved into two components: $F_{sj}$ is in the direction of the bond $j$ and will cause a stretching vibration of the bond; $F_{bj}$ is perpendicular to the bond $j$ and will cause a bending vibration in the bond. Using a simple valence-force approximation for the potential, we have

$$F_{sj} = 2F_j \cos \alpha_j = k_{sj} \delta_{sj},$$

and

$$F_{bj} = 2F_j \sin \alpha_j = k_{bj} \delta_{bj},$$

where $k_{sj}$ is the stretching-force constant, $k_{bj}$ the bending-force constant, and $\delta_{sj}$ is the elongation of the bond $j$ due to the stretching force $F_{sj}$, and $\delta_{bj} = |b_j - b_C|/\theta_j$, where $\theta_j$ is the angle through which the bond is deflected due to $F_{bj}$.

The energy deposited in the bond due to stretching is

$$E_{sj} = 2m_j \omega_j^2 r_j \cos^2 \alpha_j / k_{sj}.$$  \hspace{1cm} (17)

The energy deposited in the bond due to stretching is

$$E_{sj} = 2m_j \omega_j^2 r_j \frac{\sin^2 \alpha_j}{k_{bj}} + \left( \cos^2 \alpha_j / k_{sj} \right).$$  \hspace{1cm} (18)

The energy deposited in other bonds can be calculated in a similar manner. The fraction of the rotational energy $f_j$ deposited in bond $j$ is

$$f_j = \frac{E_{sj}}{\sum_{j=1}^{N-1} E_{sj}}.$$  \hspace{1cm} (19)

The rotational-energy change which is effective in the excitation of the bond $j$ is

$$\Delta E_{sj} = f_j \Delta E_r = f_j \sum_{i=1}^{N-1} m_i (\omega \times r_i) \cdot (\omega \times r_i) + f_j [V(b_j) - V(a_j)].$$  \hspace{1cm} (20)

Potential-Energy Change Due to Inelastic Stretching

The potential-energy change of the bond $j$ due to the rotation of the molecule can be approximated by $[V(d_{ij}) - V(d_{ij0})]$, where $d_{ij}$ and $d_{ij0}$ are the $j$th bond distances before and after inelastic stretching. Using a quadratic potential function,

$$V(d_{ij}) = V(d_{ij0}) - \frac{1}{2} k_{ij} (d_{ij} - d_{ij0})^2 - \frac{1}{2} m_j (\omega \cdot r_j)^2.$$  \hspace{1cm} (21)

For a small change, $(r_j/\alpha_j)$ may be approximated by $(d_{ij}/d_{ij0})$. Hence, from Eq. (21), the potential energy of the bond is

$$V(d_{ij}) = V(d_{ij0}) - \frac{1}{2} k_{ij} (d_{ij} - d_{ij0})^2 - \frac{1}{2} m_j (\omega \cdot r_j)^2.$$  \hspace{1cm} (22)

The new equilibrium distance $d_{ij}$ is determined by

$$k_{ij} (d_{ij} - d_{ij0}) - m_j (\omega \cdot r_j)^2 (d_{ij0}^2/d_{ij}) = 0.$$  \hspace{1cm} (23)

Combining Eqs. (20), (22), and (23),

$$\Delta E_{sj} = \frac{1}{2} m_j (\omega \cdot r_j)^2 (d_{ij0}^2/d_{ij})^2 - \frac{1}{2} k_{ij} d_{ij0}^2 [(d_{ij}/d_{ij0}) - 1],$$  \hspace{1cm} (24)

and the total energy increase in bond $j$ is

$$\Delta E_{sj} = \Delta E_r + \Delta E_{vj},$$

which is obtained from Eqs. (14) and (25).

Rotational and Vibrational Excitation in a Molecule

If a momentum impulse $Q$ were acquired by an atom $N$ in a time period so short that during that period it was not transmitted to the remainder of the molecule, then $S_N = (Q/m_N) + \omega S_N$, where $\omega S_N$ is the velocity of the atom $N$ before acquiring the impulse and $S_N$ the velocity following the impulse. Thus, $\omega S_i = S_i$ for $i \neq N$. If the impulse $Q$ is large compared to the momentum associated with the atoms of a thermal-energy molecule then, $S_N = Q/m_N$ and $S_i \approx 0$ for $i \neq N$. From conservation of momentum and the definition of the space velocity,

$$\omega \times r_N + v_N = Q/m_N - Q/\sum m_i = [(\sum m_i - m_N)/(m_N \sum m_i)] Q.$$  \hspace{1cm} (26)

The first term on the left-hand side of Eq. (26) describes the rotational effect and $v_N$ the vibrational effect of $Q$ on the $N$th atom.

We may resolve $Q$ into a component $Q_R$ which is perpendicular to $r_N$ and results in a rotation of the
molecule and into a component \( Q_v \) which will be in a random direction and will result in a vibration in the molecule which is dependent on the strength of the bonds and the moments of inertia.

Equation (26) can be separated into

\[
\begin{align*}
\omega \times r_N &= \left[ \left( \sum m_i - m_N \right) / m_N \sum m_i \right] Q_R, \\
v_N &= \left[ \left( \sum m_i - m_N \right) / m_N \sum m_i \right] Q_v.
\end{align*}
\]

Realizing that there exists the relationships \( r_N \perp \omega \) and \( r_N \perp Q_R \), it follows that

\[
\omega = \left( \sum m_i - m_N \right) / m_N \sum m_i \left( Q_R \times r_N \right) / r_N^2.
\]

For \( k \neq N \),

\[
v_k = - \frac{Q_v}{\sum m_i} - \sum m_i - m_N \left( Q_R \times r_i \right) \times r_i.
\]

Consequently, the vibrational-energy increase in bond \( N \) is

\[
\Delta E_{vN} = \frac{1}{2} \sum m_i - m_N \left( Q_v^2 + (Q_v \cdot Q_R) \right)
\]

\[
\times \left[ \sum m_i r_i^2 - \left( \sum m_i - m_N \right) (r_C \times r_N) \right] / \sum m_i r_i^2
\]

\[
+ \sum m_i - m_N \left( r_C \times Q_R \right) \left( r_N \times Q_v \right) / r_N^2.
\]

In order to resolve \( Q \) into \( Q_R \) and \( Q_v \) we define the molecular-coordinate system \((x, y, z)\) choosing the center of mass \( G \) as the origin, and placing the bond \( N \) parallel to the \( z \) axis. The vector \( Q \) is resolved into \( Q_y, Q_t, \) and \( Q_r \), where \( Q_y \) is parallel to the \( y \) axis, and \( Q_t \) and \( Q_r \) is in the direction of the \( r_N \). Since \( Q \) passes through the center of mass \( G \), it will not effect the rotation of the molecule. \( Q_y \) will cause both a bending vibration of bond \( N \) and a rotation of the molecule, particularly in \( x \) and \( z \) directions, i.e., \( \omega_y \) and \( \omega_z \), \( Q_t \) will also cause both a bending and a stretching vibration of bond \( N \) as well as a rotation in \( y \) direction \( \omega_y \). Let us write

\[
Q_v = Q_{vy} + Q_{yr},
\]

and

\[
Q_t = Q_{ty} + Q_{tr},
\]

where \( Q_{vy} \) and \( Q_{ty} \) are momenta effective in the vibration of the bond \( N \) and \( Q_{yr} \) and \( Q_{tr} \) are momenta effective in the rotation of the molecule. We define the constants as given

\[
F_{vy} = Q_{vy}^2 / Q_v^2,
\]

\[
F_{yt} = Q_{yt}^2 / Q_t^2,
\]

\[
F_{yr} = Q_{yr}^2 / Q_r^2.
\]

Upon averaging we obtain

\[
\langle Q_i^2 \rangle_i = \frac{1}{2} \left( 1 + F_{vy} + F_{yt} \right) Q_i^2
\]

and

\[
\langle Q_i \cdot Q_j \rangle_i = \frac{1}{2} \left( \left( F_{vy} F_{yt} \right) + \left( F_{yt} F_{yt} \right) \right) Q_i Q_j.
\]

based on the fact that \( \langle Q_i^2 \rangle_i = \langle Q_i \rangle_i = \frac{1}{2} Q_i^2 \). Defining as \( \gamma \) the angle between \( r_C \) and \( r_N \), the vibrational-energy increase in bond \( N \) is

\[
\Delta E_{vN} = \frac{1}{2} \sum m_i - m_N \left( \sum m_i - m_N \right) / \sum m_i \left[ 1 + F_{vy} + F_{yt} \right]
\]

\[
+ \left[ \left( F_{vy} F_{yt} \right) + \left( F_{yt} F_{yt} \right) \right] / \sum m_i
\]

\[
\times \left[ m_N - \left( \sum m_i - m_N \right) (r_C / r_N) \cos \gamma \right] / \sum m_i.
\]

It can be shown that when \( r_y = a_N \),

\[
\langle \omega_i \omega_j \rangle_h = \langle \omega_i \omega_j \rangle_h = \langle \omega_i \omega_j \rangle_h = 0.
\]

Also,

\[
\langle \omega_i \rangle_h = \frac{Q_i / 3 m_N \sum m_i - m_N}{ \sum m_i} F_{yt} / m_N a_N^2.
\]

The total energy change in bond \( N \) will therefore be

\[
\Delta E_{vN} = \frac{1}{6 m_N} \left( \sum m_i - m_N \right) / \sum m_i \left[ 1 + F_{vy} + F_{yt} \right]
\]

\[
+ \left[ \left( F_{vy} F_{yt} \right) + \left( F_{yt} F_{yt} \right) \right] / \sum m_i
\]

\[
\times \left[ m_N - \left( \sum m_i - m_N \right) \left( a_N / a_N \right) \cos \gamma \right] / \sum m_i
\]

\[
+ F_{yt} (I_{xy} \cos^2 \alpha_N + I_{yy} \sin^2 \alpha_N) + F_{yt} I_{yy}
\]

\[
\times \left( (d_N / d_N \right) [2 - \left( d_N / d_N \right)]).
\]

**Estimation of Constants**

Consider \( Q_t \) acting on the atom \( N \) as depicted in Fig. 2. As a result of \( Q_t \), the molecule will rotate and
the inertia opposing rotation will be \( I_{yy} \). As a result of \( Q_{v} \), the molecule will vibrate. The bond \( N \) will stretch and bend as a result of \( Q_{v} \) sine \( \alpha_{N} \) and \( Q_{v} \) cosine \( \alpha_{N} \), respectively. If \( \delta_{N} \) is the maximum elongation of bond \( N \) due to \( Q_{v} \) sine \( \alpha_{N} \), by energy balance we have

\[
Q_{v}^{2} \sin \alpha_{N} / m_{N} = k_{N} \delta_{N}^{2}.
\]

Similarly,

\[
Q_{v}^{2} \cos \alpha_{N} / m_{N} = k_{N} \delta_{N}^{2}.
\]

The degree of difficulty in deforming a bond increases as \( m_{N} \), \( \delta_{N} \), and \( \delta_{N}^{2} \) increase. Let us assume that the deformation inertia opposing \( Q_{v} \) is

\[
m_{N}(\delta_{N}^{2} + \delta_{N} \alpha^{2}) = Q_{v}^{2}(\cos^{2} \alpha_{N} + \sin^{2} \alpha_{N}) = k_{N} \alpha^{2},
\]

where

\[
\frac{1}{k_{N}} = \frac{\cos^{2} \alpha_{N} + \sin^{2} \alpha_{N}}{k_{N} \alpha^{2}}.
\]

(41)

The total inertia opposing \( Q_{v} \) is therefore

\[
[I_{yy} + (Q_{v}^{2}/k_{N})].
\]

The fraction of inertia that is opposing \( Q_{v} \) should also be the fraction of \( Q_{v} \) that is associated with \( Q_{v} \). Thus,

\[
\frac{I_{yy}}{I_{yy} + (Q_{v}^{2}/k_{N})} = \frac{Q_{v}}{Q_{v} + (Q_{v}^{2}/k_{N})}.
\]

(42)

Solving Eq. (42) for \( Q_{v} \), it is found that

\[
F_{v} = \frac{Q_{v}}{Q_{v} + (Q_{v}^{2}/k_{N})} = \frac{\frac{1}{2}((1 + (1 + u_{v})^{1}) + [1 - (1 + u_{v})])}{1 + (1 + u_{v})}
\]

(43)

where \( u_{v} = 4k_{N}I_{yy}/9Q_{v}^{2} \). In a similar manner,

\[
F_{v} = \frac{Q_{v}/Q_{v}^{2} = \frac{1}{2}((1 + (1 + u_{v})^{1}) + [1 - (1 + u_{v})])}{1 + (1 + u_{v})}
\]

(44)

where

\[
u_{v} = [4k_{N}(I_{xx} \cos^{2} \alpha_{N} + I_{xx} \sin^{2} \alpha_{N})] / 9Q_{v}^{2}.
\]

**FAILURE TO BOND RUPTURE**

When \( \Delta E_{BN} \) attains the value of the dissociation energy of bond \( N \) \( E_{BN} \), bond rupture results. Rearranging Eq. (40), the momentum required for bond rupture will be

\[
Q = \left[ \frac{6m_{N}E_{BN}}{(F_{v} + F_{v}) \cos^{2} \alpha_{N}[B - d_{N}^{*}2(2-d_{N}^{*})]} \right]^{1/2} \times \sum \frac{m_{i}}{m_{N}},
\]

(45)

and

\[
B = \frac{1}{(F_{v} + F_{v}) \cos^{2} \alpha_{N}} \left[ \sum m_{i} \left[ (1 + F_{v} + F_{v}) \right] + \left[ (F_{v} + F_{v}) \right] \times \frac{m_{i} - (m_{i} - m_{N}) (ac_{i} / ac_{N}) \cos \gamma} {m_{N} - (m_{i} - m_{N}) (ac_{i} / ac_{N}) \cos \gamma} \right] \times \sum \frac{m_{i}}{m_{N}},
\]

(47)

From Eqs. (24) and (45), \( B \) can also be evaluated in terms of the expression

\[
B = \frac{2E_{BN}(d_{N}^{*})^{4}}{k_{N}d_{N}^{*}(1 - d_{N}^{*})} + d_{N}^{*2}(2 - d_{N}^{*}).
\]

(48)

In the particular case where the atom receives a gamma-ray momentum impulse, the energy of the gamma ray required for bond rupture is \( E_{v} = Q/\gamma \), where \( \gamma \) is the velocity of light.

**CALCULATION OF \( Q \)**

To calculate the recoil momentum required for bond rupture, we used a method of successive approximations. The steps were: (1) calculating \( l_{xx}, I_{yy}, I_{zz}, \cos \alpha_{N} \), and \( \cos \gamma \) for each molecule using bond-distance and bond-angle data; (2) assuming a value of \( Q \); (3) calu-
lating \( u_{n} \) and \( u_{t} \) and consequently, \( F_{n} \), \( F_{r} \), \( F_{t} \), \( F_{n} \), and \( B \) using the assumed value of \( Q \) and Eqs. (43), (44), and (47); (4) solving for \( d_{N}^{*} \) in Eq. (48), using the value of \( B \) obtained in step 3, (5) calculating \( Q \) by substituting the calculated values of \( F_{n} \), \( F_{r} \), \( B \), and \( d_{N}^{*} \) into Eq. (45) and then comparing with the assumed value of \( Q \).

The minimum net recoil energies, \( E_{R} = (Q)^2/2m_N \), required for bond rupture were calculated for a series of halomethanes and are listed in Table I. It is noted that, in general, the heavier the mass of the radical attached to the activated atom, the smaller the net recoil energy required for bond rupture.

Also presented in Table I, as a percent of \( E_{R} \), are the rotational- and vibrational-excitation energies received by the bond (\( E_{BN} = E_{R} + E_{P} \)), the recoil kinetic energies of the activated atom and the radical to which it was bonded, and the internal energy of the radical. For a diatomic molecule, Steinwedel and Jensen have shown that \( E_{R}/(E_{R}+E_{P}) = \frac{3}{8} \). Typical values of this quantity for the compounds in Table I are: \( CH_3Br - 0.79 \), \( CD_2Br - 0.84 \), \( CF_2Br - 0.98 \), \( CCl_2Br - 1.00 \), \( CBr_2 - 1.00 \). It is seen that the heavier the radical attached to the activated atom, the more unlikely is rotational excitation. This is to be expected since (1) an increase in molecular weight is accompanied by an increase in the moments of inertia, and (2) the bending-force constants for similar carbon-halogen bonds do not change appreciably. The net result is, that with increased molecular weight, rotation of the molecule becomes more difficult in comparison to the vibration of the molecule.

**ENERGY OF RADICALS**

Of the net recoil energy \( E_{R} \) imparted to an atom, only a fraction of this energy is consumed in the bond rupture. Because the chemical reactivity of the radicals frequently depends upon their kinetic energy, it is of interest to determine the energies associated with the radicals.

If the net momentum \( Q \) exceeds that required for bond rupture \( Q_{0} \) the total energy available to the newly formed radicals following bond rupture is the difference between the net-recoil energy acquired by the molecule \( E_{R} = Q^2/2m_N \) and the bond dissociation energy \( E_{BN} \). The total kinetic energy acquired by the two radicals is equal to the kinetic energy of the parent molecule, \( Q^2/2 \sum m_i \) plus the bond-excitation energy which is in excess of the bond-dissociation energy, \( \Delta E_{BN} \). The internal energy \( E_{BN} \) associated with the radical, originally bonded to the activated atom, will therefore be equal to the total energy minus the bond-dissociation energy minus the kinetic energy of the radicals. Thus,

\[
E_{R} = \frac{Q^2}{2m_N} - E_{BN} = \left[ \frac{Q^2}{2 \sum m_i} + \Delta E_{BN} - E_{BN} \right] = \left[ \frac{\sum m_i - m_N}{2m_N \sum m_i} - \frac{E_{BN}}{(Q)^2} \right] Q^2, \tag{49}
\]

where \( \Delta E_{BN} = E_{BN} Q^2/(Q)^2 \).

The velocity of the activated atom is \( V_N = \frac{R + V_B}{m_N} \) and that of the radical \( V_R = \frac{R + V_{BR}}{m_N} \). Because of conservation of momentum, \( V_{BR} = \frac{\sum m_i - m_N}{m_N} \frac{V_B}{m_N} \). As a result of the conservation of energy, the energy associated with the activated atom is

\[
\langle E_{R} \rangle = \frac{m_N}{\sum m_i} \left[ \frac{Q^2}{2 \sum m_i} + \sum m_i - m_N \right] \left[ \frac{Q^2}{(Q)^2 - 1} \right] E_{BN} \tag{50}
\]

and that of the radical originally bonded to the activated atom is

\[
\langle E_{BR} \rangle = \frac{\sum m_i - m_N}{\sum m_i} \left[ \frac{Q^2}{2 \sum m_i} + \sum m_i - m_N \right] \times \left[ \frac{Q^2}{(Q)^2 - 1} \right] E_{BN}. \tag{51}
\]

The energy of the radicals as a function of the net recoil energy received by \(^{80}Br\) in \( CH_3Br \) is presented in Fig. 3. It is noted that the energies of the radicals are approximately a linear function of the net recoil energy \( E_{R} \). Thus, once the energy distribution between the radicals at the minimum recoil energy \( E_{R}^0 \) is known, the general trend of the energy distribution as a function of the net recoil energy \( E_{BR} \) can be predicted. For a series of halomethanes, there are presented in Table I the energy distribution between the radicals evaluated at \( E_{R}^0 \); these values, therefore, represent the minimum kinetic energies \( \langle E_{R}^0 \rangle \) of the radicals.

**BETA-RAY RECOIL**

The emission of a beta particle in nuclear decay will result in a recoil momentum being imparted to the isotope. For example, the maximum \(^{14}C\) beta-ray energy is 0.155 MeV; a beta ray of this energy will result in \( E_{R} = (1.55 \times 10^6)/(14.01) \) = 0.02 Mev. The methods outlined above can be used to calculate the minimum recoil energy \( E_{R}^0 \) required for \(^{14}N\) disassociation. If the beta spectrum is known, it is possible to determine the fraction of the nuclear disintegrations which will result in bond rupture.
Such calculations are being performed for $^{14}$CO$_2$, $^{14}$C$_2$H$_6$, and various tritiated compounds. The results will be reported in a separate communication.

**SUMMARY**

A molecule is visualized as being composed of a group of point-mass atoms joined together by springs. When one of the atoms in the molecule receives a momentum impulse $Q$, the atom will dissociate from the molecule if $Q \geq Q^o$. An equation is derived relating $Q^o$ to the bond energy, bond angles and distances, and the masses of the atoms in the molecule.

In deriving this expression, two major assumptions are made. They are:

1. The rotational and vibrational motions of the molecule are independent and can therefore be separated.
2. The momentum impulse is acquired by the atom in a time period which is short compared to the time required for dissociation of the atom. This dissociation time is probably of the order of $10^{-14}$ sec, the time required for one vibration. This is, perhaps, the most crucial assumption, leading to the approximation that atoms, other than the recoiling atom, do not experience an increase in space velocity. It is not obvious how to correct for this effect since the time sequence of momentum transfer through the molecule is not known. Since some intramolecular momentum transfer undoubtedly does occur, our calculated values of $Q^o$ must, of necessity, be low. The extent of correction needed to correct for this effect would probably depend upon the complexity of the molecule. Thus, for recoiling Br, $Q^o$ for CH$_3$Br could be closer to the correct value than would $Q^o$ for C$_2$H$_5$Br. Similarly, $Q^o$ for i-C$_3$H$_7$I could be more correct than $Q^o$ for n-C$_3$H$_7$I since, in the latter compound, the atoms, on the average, are separated from the recoiling iodine by a larger number of chemical bonds.