1954

Sound dispersion in halogen-substituted methanes

Thomas Dean Rossing
Iowa State College

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UMI
SOUND DISPERSION

IN HALOGEN-SUBSTITUTED METHANES

by

Thomas Dean Rossing

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physics

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In Charge of Major Work

Head of Major Department

Dean of Graduate College

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1954
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LIST OF SYMBOLS

Throughout this paper the following Latin letters are used as symbols:

- \( a, A, A_0 \) Beattie-Bridgman gas constants
- \( b, B, B_0 \) Molar heat capacity at constant pressure
- \( C_p \) Molar heat capacity at constant volume
- \( C_v \) \( C_v \) at frequencies below the dispersive region
- \( C_0 \) \( C_v \) at frequencies above the dispersive region
- \( C_\infty \) Effective \( C_v \) at angular frequency \( \omega \) in the dispersive region
- \( C_\omega \) Contribution to \( C_v \) made by molecular rotations
- \( C_{\text{rot}} \) Contribution to \( C_v \) made by molecular vibrations
- \( C_{\text{vib}} \) Contribution to \( C_v \) made by molecular translational motion
- \( C_{\text{trans}} \) Contribution to \( C_v \) made by atomic excitation
- \( C_{\text{atomic}} \) Molecular energy; use of subscripts \( \text{rot}, \text{vib}, \text{trans}, \text{atomic} \) is analogous to use in heat capacities
- \( D \) Diameter of colliding molecule
- \( e \) Base of natural logarithms
- \( E \) Sonic frequency
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<td>$f_{inf}$</td>
<td>Sonic frequency at which inflection point of dispersion curve occurs</td>
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<tr>
<td>$h$</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>$i$</td>
<td>$\sqrt{-1}$</td>
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<tr>
<td>I.P.</td>
<td>Imaginary part of a complex number</td>
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<tr>
<td>$k$</td>
<td>Boltzmann's constant</td>
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<tr>
<td>$K$</td>
<td>Coefficient of thermal conductivity</td>
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<td>$L$</td>
<td>Molecular mean free path</td>
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<td>$M$</td>
<td>Molecular weight</td>
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<tr>
<td>$n$</td>
<td>Ratio of $\varepsilon^*$ to $h\gamma_{\text{min}}$</td>
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<tr>
<td>$\Pi$</td>
<td>Number of molecules of gas per unit volume</td>
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<tr>
<td>$n_0$</td>
<td>Number of molecules per unit volume whose vibrations are in the ground state</td>
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<tr>
<td>$n_1$</td>
<td>Number of molecules per unit volume whose vibrations are in the first excited state</td>
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<td>$p$</td>
<td>Pressure</td>
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<td>Probability that a molecule in the first excited vibrational state be de-excited by a collision; a function of velocity or energy of approach</td>
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<td>$P_{10}$</td>
<td>Average of $P_{10}$ over the proper velocity or energy distribution</td>
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<td>$Q$</td>
<td>Number of molecular collisions per unit volume per unit time</td>
</tr>
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<td>$Q^*$</td>
<td>Number of molecular collisions per unit volume per unit time in which the relative energy of approach of the colliding molecules exceeds $\varepsilon^*$</td>
</tr>
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\( \mathcal{C}_{10} \)

Number of molecular collisions per unit volume per unit time which de-excite molecular vibrations

\( r \)

\( c/c_0 \)

Average number of collisions experienced by a molecule per second

\( R \)

Universal gas constant

\( \text{R.P.} \)

Real part of a complex number

\( s \)

Range of intermolecular forces

\( t \)

Time in seconds

\( T \)

Temperature in degrees Kelvin

\( V \)

Velocity of sound; subscripts \text{ideal} and \text{BB} indicate velocities in an ideal or a Beattie-Bridgman gas, respectively

\( V_0 \)

\( V \) at frequencies below the dispersive region

\( V_\infty \)

\( V \) at frequencies above the dispersive region

\( V_{\text{inf}} \)

\( V \) at frequency \( f_{\text{inf}} \)

\( V_{\text{complex}} \)

Complex velocity of sound

\( v \)

Relative velocity of two colliding molecules

\( \bar{v} \)

Average of \( v \) over a Maxwellian distribution

\( Z_{10} \)

Average collision lifetime of first excited state; average number of collisions necessary to de-excite a molecule in the first excited state.
The following Greek letters are used as symbols:

- $\alpha$: Steric factor; probability that a collision will take place with the molecules favorably oriented for excitation.
- $\gamma$: \( \frac{C_p}{C_v} \)
- $\epsilon$: Relative approach energy of two molecules.
- $\epsilon^*$: Minimum value of $\epsilon$ required for vibrational excitation.
- $\bar{\epsilon}$: One of the Beattie-Bridgman gas constants.
- $\Theta$: Vibrational relaxation time.
- $\lambda$: Acoustic wavelength.
- $\mu$: The reduced molecular weight of two colliding molecules.
- $\mu_{\text{visc}}$: Absorption of sound per wavelength due to viscosity and heat conduction.
- $\mu_{\text{relax}}$: Absorption of sound per wavelength due to relaxation effects.
- $\mu_{\text{max}}$: Maximum value of $\mu_{\text{relax}}$.
- $\nu$: Vibrational frequency per second; subscript $1$ denotes the lowest mode.
- $\tilde{\nu}$: \( \nu / c \); wave number per cm.
- $\pi$: \( 3.1416 \)
- $\rho$: Density in grams per liter.
- $\bar{\rho}$: \( \rho / M \); density in mols per liter.
- $\sigma$: See equation (47a).
- $\tau_c$: Effective molecular collision duration.
- $\tau_0$: Period of a molecular vibration; usually the mode of lowest frequency.
\[ \omega = 2\pi f; \text{ angular frequency of sound} \]
\[ \omega_{\text{inf}} = 2\pi f_{\text{inf}} \]
\[ \omega_{\text{max}} \text{ Angular frequency at which } \mu_{\text{max}} \text{ occurs} \]
\[ \eta \text{ Viscosity of gas} \]
INTRODUCTION

About thirty years ago, investigators in the field of ultrasonics discovered that the velocity of sound in polyatomic gases is a function of the sonic frequency. This phenomenon is known as the dispersion of sound, and may be explained on the basis of the failure of the translational, rotational, and vibrational energies of gas molecules to maintain thermal equilibrium with each other at high acoustic frequencies. An anomalously high acoustic absorption accompanies this dispersion in acoustic velocity.

Numerous investigators have measured the dispersion of sound caused by the lagging of the vibrational energy. (This is also referred to as the thermal relaxation process.) Nearly all the investigations have been made in diatomic and triatomic gases in which the vibrational relaxation time is relatively long and the region of dispersion is at easily attainable frequencies.

Advances in electronics have recently made possible the accurate measurement of acoustic velocities at very high frequencies. Considerable interest has thus been aroused in the study of dispersion due to the lag of rotational and translational energies; study of the vibrational energy lag in heavy organic gases, which also necessitates high frequency measurements, has been neglected. It is the
purpose of this paper to report some measurements of sonic
dispersion made in heavy gases, and to attempt to clarify
certain fundamental properties of the vibrational excitation
process in these gases which are poorly understood.

Construction of the Iowa State College acoustic interferometer was begun in 1950 under the sponsorship of the National Advisory Committee for Aeronautics. In 1951 the instrument was put into operation, and experiments were begun in nitrous oxide. This work is reported by Walker (1952) and in a later article by Walker, Rossing and Legvold (1954). In 1953 the interferometer was modified to permit high frequency measurements, and investigations were begun in the halogen-substituted methanes.

Relatively few references are made, in this dissertation, to the work of previous investigators. The reader who desires to read further in the field is referred to the excellent review article of Richards (1939) and a later review by Walker (1951).
THEORETICAL CONSIDERATIONS

Theory of Acoustic Dispersion

Propagation of sound

Several excellent treatments of the transmission of sound through isotropic homogeneous media are readily available in the literature of the field, so they will not be reproduced here. Among authors making such a treatment is Richards (1939), who arrives at an expression:

\[ V^2 = \left( \frac{\partial p}{\partial \rho} \right)_T + \left( \frac{\partial p}{\partial T} \right)_\rho \frac{MT}{\rho c_v}, \tag{1} \]

in which \( p \) is the pressure, \( T \) the temperature, \( c_v \) the molar heat capacity at constant volume, \( \rho \) the density and \( M \) the molecular weight. For acoustic waves whose intensity does not exceed 130 decibels the above expression is correct to better than 0.001 percent.

The equation of state of a perfect gas may be written:

\[ P = \frac{RT}{\nu} = \frac{RT \rho}{M}, \tag{2} \]

from which may be derived the partial derivatives of interest:

\[ \left( \frac{\partial p}{\partial \rho} \right)_T = \frac{RT}{M}, \text{ and } \left( \frac{\partial p}{\partial T} \right)_\rho = \frac{R \rho}{M}. \tag{3} \]

Substitution of these into (1) gives an expression for the square of the velocity in an ideal gas:

\[ V_{\text{ideal}}^2 = \frac{RT}{M} \left( 1 + \frac{\rho}{c_v} \right). \tag{4} \]
Since \( C_v + R = C_p \), and \( \frac{RT}{M} = \frac{P}{\rho} \) for an ideal gas, (4) may also be written in the familiar form:

\[
V_{ideal}^2 = \frac{Y \rho}{\rho}
\]

in which \( Y = \frac{C_p}{C_v} \).

An equation of state frequently applied to polyatomic molecules is that of Beattie and Bridgman:

\[
p = \frac{RT(v + B)(1 - \bar{\varepsilon})}{v^2} - \frac{A}{v^4},
\]

\[A = (1 - \frac{a}{b})A_0, \quad B = (1 - \frac{b}{a})B_0,
\]
a, b, A_0, B_0, and \( \bar{\varepsilon} \) being constants characteristic of a given gas. In most gases \( \bar{\varepsilon} \ll 1 \) at ordinary pressures and the term \( 1 - \bar{\varepsilon} \) is usually omitted. This equation may also be written in powers of \( \bar{\rho} = \frac{\rho}{\rho} = \frac{P}{M} \):

\[
p = RT\bar{\rho} + (RTB_0 - A_0)\bar{\rho}^2 + (A_0a - RTB_0b)\bar{\rho}^3 + \ldots
\]

Substitution of (7) into (1) will produce an expression for the square of the velocity in a Beattie-Bridgman gas:

\[
V_{BB}^2 = \left[ RT + 2\bar{\rho}(RTB_0 - A_0) + 3\bar{\rho}^2(A_0a - RTB_0b) \right]
+ \frac{\bar{\rho}^2RT}{MC_v} \left[ 1 + 2\bar{\rho}B_0 + \bar{\rho}^2(B_0^2 - 2B_0b) \right].
\]

Terms in \( \bar{\rho}^3 \) and higher have been omitted. Note that as \( \bar{\rho} \) becomes very small, (8) reduces to (4).

Until about 30 years ago it was believed that (4) and (8) described the velocity of sound at all frequencies. Pierce (1925) was the first to observe experimentally that the velocity of sound is not constant with frequency through-
out all frequencies. He observed that at frequencies of about $10^5$ cycles per second the velocity of sound increases above that value predicted by (4). Herzfeld and Rice (1928) explained this anomalous behavior by suggesting that at high frequencies the vibrational and translational modes fail to maintain thermal equilibrium with each other.

In any molecule the total energy $E$ may be resolved into several terms:

$$E = E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{atomic}} \quad (9)$$

The terms in the above equation represent the contributions of translatory motion, internal vibrations and rotations, and intra-atomic energy to the energy of the molecule. Since $C = \frac{dT}{dE}$, the heat capacity may also be decomposed into additive terms each corresponding to a similar term in (9).

$$C_v = C_{\text{trans}} + C_{\text{vib}} + C_{\text{rot}} + C_{\text{atomic}} \quad (10)$$

The value of each quantity depends upon temperature, and according to the Equipartition Theorem of energy, in a body at equilibrium the energy (and therefore the heat capacity) must be distributed among these terms in a definite manner. At room temperatures most atoms are in their ground state and $C_{\text{atomic}}$ is negligible. If the equilibrium between these types of internal energy is disturbed, each mode again approaches its equilibrium value at a rate characterized by its own relaxation time. Relaxation times for rotational energy are less than $10^{-8}$ second. Vibrational relaxation
times cover the range $10^{-2}$ to $10^{-10}$ second.

As long as thermal disturbances occur slowly, $G$ is correctly given by (10). As the period of a disturbance is shortened so as to be of the order of one of these relaxation times (as happens when a sound wave of high frequency is incident), the equilibrium process is unable to follow the rapid thermal cycle and the net effect is that a part of the heat capacity drops out completely. Thus $G_V$ and $V^2$ depend upon frequency throughout the dispersive region.

An additional dispersive region has been observed at frequencies so high that the wavelength of the sound approaches the molecular mean free path. First predicted by Prizmkoft (1942), this effect has been observed by Greenspan (1950) and others.

If $C_0$ denotes the heat capacity at constant volume below the dispersive region and $C_\infty$ the heat capacity above this region, then:

$$C_\infty = C_{\text{trans}} + C_{\text{rot}}, \quad (11)$$

and

$$C_o = C_\infty + C_{\text{vis}}. \quad (12)$$

Following the technique of Richards (1939), the heat capacity at acoustic angular frequency $\omega$ within the dispersive region may be written:

$$C_\omega = C_\infty + \frac{C_0 - C_\infty}{1 + i\omega \Theta}, \quad (13)$$
\( \Theta \) being the appropriate relaxation time and \( \omega \) being \( 2\pi \) times the acoustic frequency \( \tau \). Substitution of (11), (12), and (13) into (4) yields:

\[
\nu^2 = \frac{RT}{M} \left( 1 + \frac{R}{C_\infty} \right),
\]

(14)

\[
\nu_0^2 = \frac{RT}{M} \left( 1 + \frac{R}{C_0} \right),
\]

(15)

\[
\left\langle \nu_\omega \right\rangle_{\text{complex}}^2 = \frac{RT}{M} \left[ 1 + R \frac{C_\infty + \omega^2 \Theta^2 C_\infty + i(C_\infty - C_0) \omega \Theta}{C_0^2 + \omega^2 \Theta^2 C_\infty^2} \right].
\]

(16)

The real part of the latter equation gives an expression for the real phase velocity:

\[
\nu_{\text{real}}^2 = \frac{RT}{M} \left( 1 + R \frac{C_\infty + \omega^2 \Theta^2 C_\infty}{C_0^2 + \omega^2 \Theta^2 C_\infty^2} \right).
\]

(17)

The inflection point of (17) may be found by differentiation:

\[
\omega_{\text{inf}} = \frac{C_\infty}{C_0 \Theta}.
\]

(18)

Similarly, substitutions into (8) yield equations analogous to (14), (15) and (17) for a Beattie-Bridgman gas, the latter one being:

\[
\nu_{BB}^2 = \frac{1}{M} \left[ RT + 2\tilde{\beta} (RTB_0 + A_a) + 3\tilde{\beta}^2 (A_a a - RT B_0 b) \right]
\]

\[
+ \frac{R^2}{M} \left[ 1 + 2\tilde{\beta} B_0 + \tilde{\beta}^2 (B_0^2 - 2B_0 b) \right] \left[ \frac{C_\infty + \omega^2 \Theta^2 C_\infty}{C_0^2 + \omega^2 \Theta^2 C_\infty^2} \right].
\]

(19)

Since the experiment described in this dissertation involves only the vibrational relaxation time, the terms "dispersive region" and "relaxation time" will from here on refer only to the lagging of the vibrational energy.
Vibrational relaxation usually occurs over a range of about six octaves, and of course exists in a different range for each gas or gas mixture.

Absorption

The absorption of sound in gases may be due to two causes: energy losses due to viscosity and heat conduction, and losses from the non-equilibrium conditions in relaxation effects. The intensity absorption per wavelength due to the former cause, often referred to as the "classical absorption" is described by the Stokes-Kirchhoff equation:

\[ \mu_{cl} = \frac{2\pi^2 f}{\rho V^2} \left( \frac{4}{3} \eta + \frac{\gamma - 1}{C_p} k \right) \]  \hspace{1cm} (20)

In (20), \( V \) represents the velocity of sound, \( \eta \) the viscosity, \( K \) the thermal conductivity and \( \rho \) the density.

In a more recent paper by Skudrzyk (1949), consideration of the effects of "compressional viscosity" results in a small modification in (20). Skudrzyk's expression is:

\[ \mu_{cl} = \frac{2\pi^2 f}{\rho V^2} \left( 2 \eta + \frac{\gamma - 1}{C_p} k \right) \]  \hspace{1cm} (21)

The relaxation absorption, according to Richards (1939), is given by:

\[ \mu_{relax} = \frac{2\pi \Re \left( \frac{V_{com}}{V_{vcom}} \right)}{R \Re \left( \frac{V_{vcom}}{V_{com}} \right)} \]  \hspace{1cm} (22)

Substitutions from (16) into (22) give:

\[ \mu_{relax} = \frac{2R(C_0 - C_\infty) \omega \theta \pi}{\omega^2 \theta^2 C_\infty (C_\infty + R) + C(C_\infty + R)} \]  \hspace{1cm} (23)
This expression will have a maximum at a frequency given by:

\[ \omega_{\text{max}} = \frac{V_0 C_0}{V_\infty C_\infty \theta} \]  

(24)

The value of \( \mu \) relax at this maximum will be:

\[ \mu_{\text{max}} = \pi \left( \frac{V_\infty}{V_0} - \frac{V_0}{V_\infty} \right) \]  

(25)

The above expressions, of course, assume ideal gas behavior. The use of Beattie-Bridgman corrections at ordinary pressures produces very small corrections to the values of absorption calculated from (20), or (21) and (23).

The velocity dispersion and absorption are plotted in Figure 1. It may be noted that the inflection point of the velocity curve and the maximum of the dispersion curve are displaced slightly in frequency from each other.

In very accurate acoustic work the measured velocities should be corrected for the effect of absorption. In the experiments reported, the change in observed velocity because of absorption was found to be smaller than errors in measurement, and no such correction was made.

**Multiple dispersion**

In general the relaxation time of vibrations in molecules depends upon the amount of energy necessary to excite them and hence upon their vibrational frequencies. Diatomic molecules have large natural frequencies and hence
exhibit a very long relaxation time. The dispersive region for oxygen, for example, lies well within the audible range of frequencies. Polyatomic molecules, on the other hand, have rather short relaxation times.

Thus far it has been tacitly assumed that for a given gas, the relaxation process may be characterized by a single relaxation time $\Theta$. This is equivalent to assuming that all modes of vibration are excited with the same relaxation time, and furthermore that all vibrational transitions occur with the same relaxation time as transitions from the ground state to the first excited state. That all transitions between the states of a given mode of vibration have the same relaxation time has been shown by Landau and Teller (1936). If, however, the coupling between different modes of vibration is so weak that they must be excited independently by collisions and therefore possess different relaxation times, a step shaped velocity dispersion curve would result. Multiple peaks would also occur on the absorption curve plotted from (23).

Some evidence in favor of the existence of multiple dispersive regions has been reported. Pielmeier (1943) and Buschmann and Schäfer (1941) have reported a possible second step on the velocity dispersion curve of carbon dioxide. Alexander and Lambert (1942) found three dispersive regions in acetaldehyde. A later article by Lambert
and Rowlinson (1950), however, points out that the multiple
dispersions of velocity are due to errors in calculation
resulting from an ungrounded assumption that dimerization
equilibrium does not keep pace with the acoustic cycle.
Nothing is said, in this latter paper, about the multiple
absorption peaks also reported earlier.

Great difficulty would be experienced in the observation of multiple dispersive regions in triatomic molecules,
if indeed such exist. At room temperature one mode usually accounts for most of the vibrational contribution to specific heat. Any steps on the velocity dispersion curve due to the other modes would be so small that they would be difficult to detect.

Detection of multiple dispersion due to a lack of intermodal coupling, if it exists, might be most probable in molecules such as the halogen-substituted methanes having several modes of low frequency which can be excited at room temperatures. On the other hand, if intermodal coupling is strong enough so that energy is transferred readily from one mode to another, only a single relaxation time will be observed. Presumably this will be the relaxation time of the mode of lowest frequency.
Trace catalyst effect

A remarkable phenomenon which has been observed in connection with relaxation time studies is the "trace catalyst" effect. Collisions between unlike molecules are sometimes much more efficient in the excitation of vibrations than those between like molecules. Knudsen and Fricke (1940), for example, found that less than 20 collisions between carbon dioxide and water vapor molecules are necessary, on the average, to excite molecular vibrations in carbon dioxide. However, more than 50,000 collisions between two carbon dioxide molecules are necessary for the excitation of one of them. Other catalytic pairs are cited by Walker (1951).

Several explanations of the trace catalyst effect have been offered. Eucken and Becker (1934) observed that in a collision between two molecules which have a chemical affinity for each other the probability of vibrational excitation is large. Landau and Teller (1936) suggest that excitation is more probable when the two colliding molecules approach each other at a high velocity, thus explaining the effectiveness of hydrogen and helium as catalysts.

The addition, to a test gas, of small concentrations of another gas may have two different effects upon the relaxation time. If the added gas serves as a catalyst,
the relaxation time will be shortened, since fewer collisions will be required for excitation. If, on the other hand, collisions between the unlike molecules are less effective in exciting vibrations than those involving two molecules of the test gas, then the opposite will take place. At a given pressure and temperature, fewer collisions between two test gas molecules will occur due to the presence of the added molecules, and the relaxation time will be lengthened.

**Multiple collisions**

In general a certain average number of collisions are required to excite or de-excite the molecular vibrations in a given gas. Since the number of binary collisions is proportional to the pressure of the gas, it follows that the relaxation time will be inversely proportional to the pressure when binary collisions are responsible for vibrational excitation. If triple collisions are primarily responsible, the relaxation time will be inversely proportional to the square of the pressure and so forth.

In equations such as (17) and (23) dealing with acoustic dispersion, the independent variable is invariably $\omega \Theta$ rather than $\omega$. Hence if the relaxation time $\Theta$ is inversely proportional to pressure, the dispersion curve may well be
drawn with log \( f/p \) as the abscissa instead of log \( f \). This is a great advantage in experimental work since it provides a method of obtaining a continuous range of "frequencies" without changing the frequency of the sound source. Of course it must first be ascertained which type of collisions is responsible for vibrational excitation so that the correct pressure dependence is used.

No conclusive evidence has been presented supporting any importance of collisions of orders above the second. Walker (1951) suggested that certain data of previous investigators, involving COS with added quantities of He and Ar, might be interpreted on the basis that triple collisions are of greater importance than the binary type. Walker, Rossing and Legvold (1954) later report that triple collisions are not important in the excitation by He, Ar and \( \text{N}_2 \) of \( \text{N}_2\text{O} \) which is very similar in structure to COS.
Relaxation theory

A gas will be considered which has \( n_1 \) molecules with vibrations in the first excited state and \( n_0 \) molecules with vibrations in the ground state per unit volume. If at all times \( n_0 + n_1 = \bar{n} \), a constant, the continuous exchange of molecules between states 0 and 1 may be characterized by the equation:

\[
\frac{dn_i}{dt} = f_{01} n_0 - f_{10} n_i,
\]

in which \( f_{01} \) specifies the number of \( 0 \rightarrow 1 \) transitions per ground state molecule per second and \( f_{10} \) the corresponding number of \( 1 \rightarrow 0 \) transitions per excited molecule.

When the gas is in equilibrium, \( \frac{dn_i}{dt} = 0 \), and therefore, according to the principle of detailed balancing, the total numbers of transitions in each direction are equal. At equilibrium:

\[
\bar{n}_i = n_0 e^{-h\nu/kT},
\]

and so:

\[
f_{01} = f_{10} e^{-h\nu/kT}.
\]

In the above equations \( h \) and \( k \) are the Planck and Boltzmann constants respectively, \( \nu \) is the frequency of molecular vibrations and \( T \) is the temperature in degrees Kelvin.

Since \( \bar{n} = n_0 + n_1 \) at all times, (26) may be written:
\[
\frac{dn}{dt} + n \left( v_{01} + v_{10} \right) = v_{01} \bar{n} \tag{29}
\]

Since \( \bar{n} \) is constant, the solution to this differential equation for non-equilibrium is:

\[
n_t = c_1 + c_2 e^{-\left( v_{01} + v_{10} \right) t} \tag{30}
\]

The relaxation time of this process can then be seen to be:

\[
\Theta = \frac{1}{v_{01} + v_{10}} \tag{31}
\]

\( \Theta \) is the time necessary for the departure from thermal equilibrium to be reduced to 1/e of its initial value.

Some authors erroneously assume that \( h \sqrt{v/kT} \gg 1 \) and \( f_{10} \ll f_{10} \), and hence that \( \Theta \approx 1/f_{10} \). At vibrational frequencies less than about \( v = 1.5 \times 10^{13} \text{ sec}^{-1} \) (corresponding to \( \tilde{v} = 500 \text{ cm}^{-1} \) in spectroscopic wave numbers, since \( \tilde{v} = \sqrt{v/c} \)), this assumption is ungrounded.

Kennard (1938) writes an expression for the total number of collisions \( R \) that a molecule makes, on the average, per second:

\[
R = \sqrt{\pi} \bar{n} D^2 \tilde{v} \tag{32}
\]

In (32) \( \bar{n} \) is again the number of molecules per unit volume, \( D \) is the effective molecular diameter and \( \tilde{v} \) is the average molecular velocity. Using the same notation, the mean free path \( L \) may be written:

\[
L = \frac{1}{\sqrt{\pi} \bar{n} D^2} \tag{33}
\]

and the viscosity \( \eta \):

\[
\eta = 0.499 \rho \tilde{v} L \tag{34}
\]
The average velocity for a Maxwellian distribution of molecules is:

\[ \bar{v} = \sqrt{\frac{8RT}{\pi M}}. \]  

(35)

Combining (32), (33), (34) and (35) gives the collision rate \( R \) in \( \text{sec}^{-1} \) in terms of the viscosity \( \gamma \) in centipoise:

\[ R = \frac{128 \pi \times 10^3}{\eta}. \]  

(36)

Four more quantities, which are of interest in this theory, \( Z_{10}, Z_{01}, P_{10}, \) and \( P_{01} \), will now be defined. \( P_{01} \) and \( P_{10} \) are the probabilities that a molecule in the ground or first excited state, respectively, will be excited or de-excited in collision. \( Z_{01} \) and \( Z_{10} \) are the mean collision lifetimes of the ground and first excited states, respectively; in other words they are the numbers of collisions the states of interest are able to survive. It is then clear that:

\[ Z_{01} = \frac{1}{P_{01}}, \quad \text{and} \quad Z_{10} = \frac{1}{P_{10}}. \]  

(37)

Also:

\[ f_{01} = P_{01}R, \quad \text{and} \quad f_{10} = P_{10}R. \]  

(38)

Substitution of (28) and (38) into (31) gives:

\[ \Theta = \frac{1}{f_{10}(1+e^{-h\nu/kT})} = \frac{1}{R_0 R (1+e^{-h\nu/kT})}. \]  

(39)

By (37):

\[ Z_{10} = \Theta R (1+e^{-h\nu/kT}). \]  

(40)

Similarly, multiplication of both sides of (28) by \( e^{h\nu/kT} \) and substitution of it and (38) into (31) yields:
\[
\begin{align*}
\Theta &= \frac{1}{f_{01} (1 + e^{\hbar \omega / kT})} = \frac{1}{\Gamma P_{01} (1 + e^{\hbar \omega / kT})}. \quad (41)
\end{align*}
\]

By (37) we obtain:
\[
Z_{01} = \Theta \Gamma (1 + e^{\hbar \omega / kT}). \quad (42)
\]

Division of (42) by (40) gives the relation:
\[
\frac{Z_{01}}{Z_{10}} = \frac{1 + e^{\hbar \omega / kT}}{1 + e^{-\hbar \omega / kT}} \quad \text{or} \quad (43)
\]

In case \( \hbar \omega / kT \gg 1 \) (corresponding to \( \omega \gg 500 \text{ cm}^{-1} \)):
\[
Z_{01} \approx Z_{10} e^{\hbar \omega / kT}. \quad (44)
\]

In case \( \hbar \omega / kT \ll 1 \), which is not realizable at ordinary temperatures:
\[
Z_{01} \approx Z_{10}. \quad (45)
\]

**Prediction of \( P_{10} \)**

Several authors have attempted to develop the theory of translation-vibration energy exchanges in molecular collisions. Landau and Teller (1936) use a classical approach to the problem, and develop a theory which has been very successful in explaining energy transfer probabilities in relatively simple molecules.

According to their theory, the effectiveness of a collision is determined by the ratio \( r = \tau / \tau_0 \), where \( \tau_0 \) is the effective duration of a collision and \( \tau \) is the period of a molecular vibration. In general, \( r \gg 1 \) for
vibrational excitation and the probability is therefore very small. For \( \tau \) they use the expression \( \tau = \frac{1}{2\pi \nu} \), \( \nu \) being the vibrational frequency. (They explain the use of the \( 2\pi \) by saying that frequency is usually introduced into physical formulae by differentiating expressions such as \( \sin 2\pi \nu t \).) The collision duration may be written \( \tau = s/v \), \( s \) being the range of intermolecular forces and \( v \) the relative velocity of approach of the colliding molecules. The probability for de-excitation in a single collision when the approach velocity lies within the range \( v \) to \( v + dv \) is:

\[
P(\nu) = \alpha e^{-\sigma} = \alpha e^{-\frac{2\pi \nu s}{v}}.
\]

(46)

\( \alpha \) is a steric factor which gives the probability that a collision will find the molecules favorably oriented for excitation or de-excitation. Values of \( \alpha \) usually range from \( 1/3 \) to \( 1/30 \).

Bethe and Teller (1942) integrate the above expression over a Maxwellian distribution of velocities to obtain:

\[
P_0 = C \sigma e^{-\sigma}.
\]

(47)

In this equation:

\[
\sigma = 0.090(\bar{v}s)^{\frac{1}{2}}(\frac{\mu}{\tau})^{\frac{1}{2}},
\]

(47a)

\[
C = \left(\frac{4}{3}\right)^{\frac{3}{2}} \alpha
\]

(47b)

where \( \mu \) is the reduced molecular weight of the colliding molecules, or in case the two molecules are identical, it is the molecular weight. In the above, \( s \) is measured in
Mott and Jackson and arrive at a similar expression for $P_{10}$. They point out that in case the colliding molecules have a chemical affinity for each other, the probability of energy exchange will be increased since the strong attractive force will greatly increase the relative velocity of approach.

Recent theory by Schwartz, Slawsky and Herzfeld (1952), based on the approach of Zener, makes use of an exponential repulsion and a one dimensional model. Using a quantum mechanical approach, these authors arrive at a somewhat more complicated expression for $P_{10}$ which, they point out, has essentially the same dependence upon $\mu$, $\bar{v}$, and $T$ as the classical theory of Landau and Teller.

The theories described fit the experimental data quite well for the relatively simple cases of diatomic and linear triatomic molecules. The catalytic effect of certain gases is also explained by such theory, either on the basis of a chemical affinity between the colliding molecules, or else because one of the molecules has a small mass and a high velocity.
Energy excitation theory

Recently Fogg, Hanks and Lambert (1953) have measured the vibrational relaxation times of several halo-methane vapors and have calculated the number of collisions necessary to excite the lowest modes of vibration. At least four of these gases appear to fit an empirical relation of the form:

\[ P_{oi} = e^{-x\nu_i} \]  \hspace{1cm} (48)

in which \( \nu_i \) is the frequency of the lowest vibrational mode and \( x \) is a proportionality constant characteristic of the particular group of gases. This suggests that the probability of vibrational excitation depends upon the energy of approach of the colliding molecules rather than upon the velocity of approach. An energy excitation theory, based on the above suggestion, will now be further developed by examination of the deactivation process.

It may be assumed that the probability \( p_{lo} \) of de-exciting a vibrating molecule in a given collision can be written in terms of the relative energy of approach \( \epsilon \) of the colliding molecules:

\[ p_{lo} = \alpha \quad \epsilon > \epsilon^* \]

\[ = 0 \quad \epsilon < \epsilon^* \]  \hspace{1cm} (49)

\( \alpha \), in the above equation, is the steric factor and \( \epsilon^* \) is some minimum relative energy of approach which must be exceeded in order to produce de-excitation. If it is
assumed that the mode of lowest frequency $\nu$ is the first
to be de-excited, $\epsilon^*$ may be written:

$$\epsilon^* = n \hbar \nu,$$  \hspace{1cm} (50)

where $n$ is some constant.

Fowler and Guggenheim (1949) write the following
expression for the number of collisions, $Q$, between like
molecules per unit volume per unit time in which the relative
translational energy lies between $\epsilon$ and $\epsilon + d\epsilon$:

$$Q = \frac{\pi^2}{2} \left(\frac{2 \pi k T}{M}\right)^{1/2} e^{-\epsilon/kT} 2 D^2 \frac{e^2}{kT} \frac{d\epsilon}{kT}.$$  \hspace{1cm} (51)

In (51), $D$ is the molecular diameter, $M$ the molecular
weight, and $\bar{n}$ the number of molecules per unit volume.

Integration of (51) from $\epsilon^*$ to $\infty$ gives the number of col­
lisions in which the relative energy of approach exceeds $\epsilon^*$:

$$Q^* = \frac{\pi^2}{2} \left(\frac{2 \pi k T}{M}\right)^{1/2} 2 D^2 e^{-\epsilon^*/kT} \left(\frac{\epsilon^*}{kT} + 1\right)$$

$$\hspace{1cm} = \bar{n} \alpha e^{-\epsilon^*/kT} \left(\frac{\epsilon^*}{kT} + 1\right)$$  \hspace{1cm} (52)

where $\alpha$ is the collision rate per molecule. To find the
total number of collisions per unit volume per second which
bring about de-excitation, (49) may be multiplied by (52),
since it has been assumed that $\alpha$ is not a function of
energy.

$$Q_{10} = \bar{n} \alpha e^{-\epsilon^*/kT} \left(\frac{\epsilon^*}{kT} + 1\right) = \bar{n} \alpha P_{10}.$$  \hspace{1cm} (53)

$P_{10}$, the probability that de-excitation takes place in a
single collision, may thus be written:

\[ P_{10} = e^{-\frac{e^*}{kT}} \left( \frac{e^*}{kT} + 1 \right) \]  \hspace{1cm} (54)

or by substitution from (50):

\[ P_{10} = e^{-\frac{n_h \nu_i}{kT}} \left( \frac{n_h \nu_i}{kT} + 1 \right) \]  \hspace{1cm} (55)

According to (28) and (38), the corresponding probability for excitation will then be:

\[ P_{01} = e^{-\frac{h \nu_i}{kT}} P_{10} \]

\[ = e^{-\frac{(m_1)h \nu_i}{kT}} \left( \frac{n_h \nu_i}{kT} + 1 \right) \]  \hspace{1cm} (56)

The above relations picture vibrational excitation and de-excitation as an involved process, requiring a certain minimum energy of approach. It is tempting to assume that vibrational excitation and de-excitation take place only when a molecule is able to penetrate very deeply into the force field of another, the penetration requiring a certain amount of energy. It is even possible that the collision partners form a compound molecule with a very short lifetime, during which energy may pass readily between translational and vibrational degrees of freedom. The process of formation of the compound molecule would require a certain minimum amount of energy.

Fogg, Hanks and Lambert (1953) have apparently treated \( P_{01} \) and \( P_{10} \) as being the same in contradiction to (56),
and several errors have resulted. It should be noted that
the minimum energies of approach required for the excitation
and de-excitation processes differ by $\hbar \nu$.

Trace catalysts may still exist for gases which obey
the energy excitation theory, but gases which catalyze
diatomic and triatomic gases may not produce the same result
in polyatomic gases. Hydrogen and helium apparently are
strong catalysts in diatomic and triatomic gases because
they have a very high velocity at ordinary temperatures.
In order to be a catalyst in a gas obeying the energy ex-
citation theory, however, a gas must be able to penetrate
the force field of another easily, or form a compound mol-
ecule readily, and have a fairly large steric factor.

Heat Capacities of Gases

According to (10), the heat capacity of a gas is made
up of contributions from molecular vibrations, rotations
and translations. At sufficiently high temperatures, each
degree of translation or rotation contributes $\frac{1}{2} R$, and
each vibrational mode contributes $R$ times the degree of
degeneracy.

At room temperatures, $C_{\text{rot}}$ is fully developed in poly-
atomic gases. Thus the rotational contribution from linear
polyatomic molecules is $R$, and the contribution from non-
linear polyatomic molecules is $3/2 \, R$, since they have moments of inertia along three perpendicular directions. Translational energy, also characterized by three degrees of freedom, contributes $3/2 \, R$.

Vibrational heat capacities, on the other hand, are rarely complete. Assuming that the molecules are perfect harmonic oscillators, the vibrational contribution to heat capacity may be written in terms of the frequencies of the $n$ modes each having a degeneracy of order 1:

$$C_{\text{vib}} = \sum_{i=1}^{n} \frac{\hbar^2 \nu_i^2 \, R}{2(\cosh \frac{\hbar \nu_i}{kT} - 1)}.$$  \hspace{1cm} (57)

Spectroscopic data indicate that molecular vibrations are not perfectly harmonic, and thus a transition from the second excited state to the first excited state does not produce the same frequency as from the first state to the ground state. Walker (1952) points out that the error in $V_0$ introduced by the neglect of this anharmonicity in calculating $C_{\text{vib}}$ is about 0.03 percent. The total heat capacity at constant volume, at room temperature and below the dispersive region in polyatomic molecules may then be given as:

$$C_o = 3R + C_{\text{vib}},$$  \hspace{1cm} (58)

where $C_{\text{vib}}$ is calculated from (57). Above the dispersive region:
\[ C_\infty = 3R \quad . \]  
(59)

In any gas:
\[ C_p - C_v = T \left( \frac{\partial p}{\partial T} \right)_v \left( \frac{\partial v}{\partial T} \right)_p \quad . \]  
(60)

For a perfect gas this reduces to:
\[ C_p - C_v = R \quad . \]  
(61)

In a Beattie-Bridgman gas, the same equation gives:
\[ C_p - C_v = \frac{R(v + B_0)}{v^2 + v(B_0 - \frac{\Delta v}{RT})} \quad . \]  
(62)

Thus, if \( C_p \) and the Beattie-Bridgman constants are known from experimental data, it is possible to check (58) above.
EXPERIMENTAL CONSIDERATIONS

Apparatus

The measurement of the velocity of sound in a medium involves the measurement of the frequency $f$ and the wavelength $\lambda$ in the medium. The velocity is given by their product. The measurement of $f$ and of $\lambda$ is done by means of an acoustic interferometer of the Pierce type.

A cross section of the acoustic chamber of the interferometer is shown in Figure 2. A gold-plated, X-cut quartz crystal is clamped in its modal plane and is driven near its frequency of resonance. An optically flat stainless steel reflector is connected to a micrometer screw by a precision ground invar rod. The micrometer screw, which was built by the Gaertner Company, has a least count of 0.001 mm. By measuring the positions of the reflector for successive standing wave patterns, acoustic wavelengths may be measured with a high degree of precision.

The crystal and the reflector are made parallel by adjusting the three leveling screws to obtain the best standing wave pattern. Parallelism is maintained by the precision bearing which allows less than 0.001 inch of sideways play as the reflector moves up and down. Parallelism within 0.1 wavelength must be maintained at all times.
to accurately measure wavelengths.

The acoustic chamber is constructed from stainless steel, all seams being silver soldered. A copper gasket pressed by sixteen bolts insures a vacuum-tight seal. The invar rod, a mercury thermometer and the oscillator leads proceed up through O-ring vacuum seals. The entire apparatus can be immersed in a constant temperature water bath or in an electric oven. In the latter case, a cooling disc, in which cold water circulates, covers the oven and protects the micrometer and the vacuum seals from high temperatures.

The crystal oscillator circuit is shown in Figure 3. It is a variation of the Pierce type of circuit, using precision components throughout, and drives the crystal at a very constant frequency and amplitude. The theory of its design is discussed by Rossing (1952). The frequency of the crystal is determined to a precision of 1 part in 10,000 by heterodyning the output of the oscillator with the signal from some convenient broadcast station to produce a beat note in the audio frequency range.

As the reflector moves up or down, the changing acoustic field causes small changes in the electrical impedance of the crystal. Sharp peaks in the impedance indicate the positions of the reflector for which standing waves result. The circuit used to measure small changes in the crystal
impedance is shown in Figure 4. Voltages from the crystal are isolated by two cathode followers, independently rectified and fed into an unbalanced d.c. amplifier. A biased microammeter with five ranges measures the changes in the output of the d.c. amplifier. A General Electric vacuum thermocouple, which generates a voltage proportional to the amount of radio frequency current through it, is used to measure the crystal current.

The impedance measuring circuit and the crystal oscillator receive their power from a power supply with an electronic voltage regulator. The regulator, which is of the degenerative feedback type, makes use of dry batteries for reference voltages. A Sorenson voltage regulator using a saturable reactor is used to protect the apparatus from fluctuations in line voltage. Provisions have been made to use an all-battery power supply, but the electronic power supply is found to be as stable as the battery supply. The power supply circuit is shown in Figure 5.

The crystals used were cut and plated by the James Knights Company and have resonant frequencies of 1000 and of 300 kilocycles per second. For most of the measurements, the 300 kilocycle crystal was used since the wavelength of the sound produced by it is over three times as great as that produced by the 1000 kilocycle crystal and is therefore easier to measure. Both crystals were made two inches
in diameter. Since this is of the order of 50 wavelengths, the acoustic waves are approximately plane.

The gas-handling system is shown schematically in Figure 6. A two stage mechanical vacuum pump is capable of evacuating the entire system to a pressure of 0.2 \( \mu \). The pressure in the acoustic chamber is measured by means of a two-meter manometer and a McLeod vacuum gauge. A drying chamber is available for use with gases which may contain water vapor as an impurity, although desiccation was not used in this experiment. Kerotest packless diaphragm valves are used throughout to close off various parts of the system. Test gases can be drawn into a liquid air cold trap and distilled into the chamber to remove traces of non-condensable gases. Before each measurement, the entire system is evacuated and outgassed to assure a gas sample of as high a purity as possible.

The temperature of the water bath is controlled by a mercury thermostat and an infra-red heating lamp. Tests made with a suitably mounted thermistor show that the temperature variation within the acoustic chamber does not exceed 0.1\(^\circ\)C.
Experimental Procedure

The velocity of sound was measured in each gas at a variety of f/p ratios, by means of the acoustic interferometer. The corresponding values of $v^2$ were then plotted on semi-logarithmic graphs in Figures 7 to 20. $v_{\text{ideal}}^2$ was plotted using (17) with an arbitrary value of $\theta$. The curve was then shifted along the f/p axis until it best fit the experimental data, since according to (17), the effect of changing $\theta$ is merely to shift the entire curve along this axis. In those gases for which the dispersive region occurred at low frequencies and for which the Beattie-Bridgman constants were known, the $v_{\text{BB}}^2$ curve has been drawn using (19). The experimental values of $v^2$ were then corrected by adding the value of $v_{\text{ideal}}^2 - v_{\text{BB}}^2$ measured along the f/p ordinate corresponding to that point.

Since $g_{\text{rot}}$ is fully developed in polyatomic gases at room temperatures, $g_{\infty}$ was then calculated from (59). $g_{\text{vib}}$ was computed using (57) and the vibrational wave numbers observed spectroscopically; $g_{\text{vib}}$ was then computed by (58). Thus the anharmonicity of the molecular vibrations was taken into account. Values of $g_{\text{vib}}$ and $g_{\text{rot}}$ are given in Table I. Experimental measurements of $c_p$ were available for a few of the gases, and $c_v$ could thus be computed.
from (62). Values of $C_0$ from (58) usually fit the experimental data better than those from (62).

Nearly every value of $V^2$ in Figures 7 to 20 was computed using the average of ten independent measurements of $\lambda$. When absorption was not too great, the distances measured corresponded to twenty nodes or half wavelengths. At large ratios of $f/p$, however, the absorption becomes large and only four or five nodes were detectable. The data at the high frequency ends of the velocity curves therefore exhibit some scatter. When high absorption necessitated taking data near the crystal, a graphical correction was made for the capacitive effect of the reflector on the crystal.

The gases used in the experiment were of the highest purity available. CHClF$_2$, CHCl$_2$F, CCl$_2$F$_2$, CH$_2$Cl, CH$_3$Br, CCl$_3$F and CClF$_3$ were purchased from the Matheson Company. OBrF$_3$, CH$_2$ClF, CH$_2$F$_2$, CBr$_2$F$_2$, CBrClF$_2$, CF$_4$ and CHF$_3$ were furnished by the Jackson Laboratory of E. I. duPont de Nemours and Company. The purities reported by the suppliers of the gases are listed in Table I. Several of the above gases were stored in cylinders as gas over liquid; these were withdrawn in their liquid phase to minimize contamination by air and non-condensable gases. Others were liquified, by use of the liquid nitrogen cold trap, and then evaporated into the system after pumping off all
<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity %</th>
<th>M</th>
<th>$\gamma$ cal/mol °K.</th>
<th>Cl°K. cal/mol °K.</th>
<th>Gvib°K. cal/mol °K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Br</td>
<td>99.4</td>
<td>94.95</td>
<td>611</td>
<td>1.03</td>
<td>2.26</td>
</tr>
<tr>
<td>CHClF₂</td>
<td>97</td>
<td>86.48</td>
<td>369</td>
<td>1.45</td>
<td>5.99</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>99.5</td>
<td>50.49</td>
<td>732</td>
<td>0.78</td>
<td>1.84</td>
</tr>
<tr>
<td>CO₂F</td>
<td>99.9</td>
<td>137.38</td>
<td>244</td>
<td>4.05</td>
<td>10.63</td>
</tr>
<tr>
<td>CBrClF₂</td>
<td>99.9</td>
<td>165.38</td>
<td>200</td>
<td>1.85</td>
<td>10.24</td>
</tr>
<tr>
<td>CF₄</td>
<td>---</td>
<td>88.01</td>
<td>437</td>
<td>2.93</td>
<td>6.91</td>
</tr>
<tr>
<td>CH₂F₂</td>
<td>99.7</td>
<td>52.03</td>
<td>532</td>
<td>1.12</td>
<td>2.22</td>
</tr>
<tr>
<td>CH₂ClF</td>
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<td>68.46</td>
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<td>1.56</td>
<td>3.46</td>
</tr>
<tr>
<td>CO₂F₃</td>
<td>99.0</td>
<td>104.47</td>
<td>356</td>
<td>3.16</td>
<td>8.16</td>
</tr>
<tr>
<td>CHCl₂F</td>
<td>99.0</td>
<td>102.93</td>
<td>274</td>
<td>1.72</td>
<td>6.76</td>
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<tr>
<td>CHF₃</td>
<td>---</td>
<td>70.02</td>
<td>508</td>
<td>2.48</td>
<td>4.78</td>
</tr>
<tr>
<td>CO₂F₂</td>
<td>97</td>
<td>120.92</td>
<td>260</td>
<td>1.76</td>
<td>8.63</td>
</tr>
<tr>
<td>CBr₂F₂</td>
<td>99.9</td>
<td>209.84</td>
<td>165</td>
<td>1.88</td>
<td>10.55</td>
</tr>
<tr>
<td>CBrF₃</td>
<td>---</td>
<td>148.93</td>
<td>297</td>
<td>4.24</td>
<td>9.84</td>
</tr>
</tbody>
</table>
non-condensible vapor. The close fit of the low frequency experimental data to the calculated values of \( v_0^2 \) demonstrates the high degree of purity of the gases used.

Values of \( f_{\text{inf}} \) were taken from the curves in Figures 7 to 20. The corresponding values of \( \Theta \) were then calculated by use of (18). After the best fit was obtained with the experimental data, the theoretical dispersion curves were further moved along the \( f/p \) axis to establish limits to the area in which the curve might reasonably lie. It was then assumed that these "reasonable limits" were 85 percent certain of containing the true dispersion curve. By means of the normal error curve, the corresponding limits for 50 percent certainty were calculated and established as the probable error for \( \Theta \). Values of \( \Theta \) appear in Table II.

Since it was observed that none of the dispersion curves showed any evidence for the existence of multiple relaxation times, it was assumed that the lowest vibration was excited with its characteristic relaxation time, and that the energy passed freely to the other modes. Thus the relaxation time of the lowest mode \( \Theta_1 \) should be given by the expression:

\[
\Theta_1 = \Theta \frac{C_i}{C_{\text{vib}}} \tag{63}
\]

in which \( C_1 \) is that part of \( C_{\text{vib}} \) corresponding to the lowest vibrational mode. Values of \( \Theta_1 \) were calculated.
### Table II

**Relaxation Times and Collision Lifetimes**

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\omega \times 10^6$ (sec.)</th>
<th>$\Theta_1 \times 10^3$ (sec.)</th>
<th>$\alpha \times 10^{-9}$ (sec.)</th>
<th>$Z_{10}$</th>
<th>$\gamma$</th>
<th>$\gamma^* M^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Br</td>
<td>7.5 ± 0.3</td>
<td>3.4 ± 0.3</td>
<td>10.79 ± 0.22</td>
<td>386 ± 14</td>
<td>611</td>
<td>328</td>
</tr>
<tr>
<td>CHClF$_2$</td>
<td>9.5 ± 0.7</td>
<td>2.2 ± 0.2</td>
<td>9.98 ± 0.20</td>
<td>268 ± 24</td>
<td>269</td>
<td>227</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>20.4 ± 1.1</td>
<td>8.6 ± 0.5</td>
<td>10.91 ± 0.22</td>
<td>966 ± 67</td>
<td>732</td>
<td>300</td>
</tr>
<tr>
<td>CCl$_3$F</td>
<td>2.0 ± 0.4</td>
<td>1.5 ± 0.2</td>
<td>11.79 ± 0.24</td>
<td>234 ± 31</td>
<td>244</td>
<td>202</td>
</tr>
<tr>
<td>CBrClF$_2$</td>
<td>5.0 ± 0.4</td>
<td>0.9 ± 0.1</td>
<td>9.66 ± 0.48</td>
<td>121 ± 15</td>
<td>200</td>
<td>188</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>75.6 ± 0.8</td>
<td>32.1 ± 0.3</td>
<td>6.84 ± 0.34</td>
<td>2450 ± 125</td>
<td>437</td>
<td>256</td>
</tr>
<tr>
<td>CH$_2$F$_2$</td>
<td>3.0 ± 0.3</td>
<td>1.5 ± 0.2</td>
<td>9.81 ± 0.49</td>
<td>159 ± 24</td>
<td>532</td>
<td>245</td>
</tr>
<tr>
<td>CH$_2$ClF</td>
<td>3.0 ± 0.1</td>
<td>0.45 ± 0.5</td>
<td>11.20 ± 0.56</td>
<td>60 ± 7</td>
<td>358</td>
<td>206</td>
</tr>
<tr>
<td>CClF$_3$</td>
<td>23.9 ± 0.6</td>
<td>9.3 ± 0.2</td>
<td>11.23 ± 0.23</td>
<td>1240 ± 37</td>
<td>356</td>
<td>237</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$F</td>
<td>2.0 ± 0.4</td>
<td>0.5 ± 0.1</td>
<td>11.48 ± 0.57</td>
<td>74 ± 15</td>
<td>274</td>
<td>198</td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>47.9 ± 1.8</td>
<td>24.9 ± 0.9</td>
<td>8.34 ± 0.42</td>
<td>2260 ± 140</td>
<td>508</td>
<td>363</td>
</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>7.8 ± 0.6</td>
<td>1.6 ± 0.1</td>
<td>10.31 ± 0.21</td>
<td>212 ± 14</td>
<td>260</td>
<td>201</td>
</tr>
<tr>
<td>CBr$_2$F$_2$</td>
<td>2.9 ± 0.3</td>
<td>0.50 ± 0.05</td>
<td>9.24 ± 0.47</td>
<td>68 ± 8</td>
<td>165</td>
<td>179</td>
</tr>
<tr>
<td>CBrF$_3$</td>
<td>19.6 ± 0.1</td>
<td>8.4 ± 0.1</td>
<td>8.05 ± 0.40</td>
<td>8.0 ± 43</td>
<td>297</td>
<td>239</td>
</tr>
</tbody>
</table>
by (63) and appear in Table II.

The collision rate $\mathcal{R}$ was calculated for each gas by means of (36), using experimental values of the viscosity $\eta$ wherever available. Since for the majority of the gases used the viscosity had not been measured, it was calculated from critical data by the empirical equation:

$$\eta = 6.30 \times 10^{-4} \left[ \frac{M^3 P^2}{T^2} \right]^{-\frac{1}{6}} \frac{(T/P)^{3/2}}{T/P + 0.8} \quad (64)$$

$T_c$ and $P_c$ in (64) represent the critical values of temperature and pressure, $T$ is the temperature and $M$ is the molecular weight. Critical data, where not available, were calculated from the boiling point and the parachor by the method of Meissner and Redding (1942). Viscosities and collision rates calculated by the above method are seldom more than five percent different from measured values. Values of $\mathcal{R}$ were arbitrarily given a probable error of two percent if calculated from experimental values of $\eta$ and five percent if $\eta$ was obtained by the use of (64).

$Z_{10}$ was calculated for each gas by means of (40), using for $\Theta$ the relaxation time of the lowest mode $\Theta_1$ calculated from (63). These values of $Z_{10}$, together with corresponding values of $\mathcal{R}$, also appear in Table II.
Experimental Results

It may be noted in Figures 7 through 20 that none of the gases measured showed multiple dispersive regions. This indicates that intermodal coupling is relatively strong in these molecules, and the assumption made by the use of (63) is justified.

Furthermore, since the use of f/p along the axis of abscissas yields the proper form of dispersion curve, the excitation and de-excitation of molecular vibrations must be brought about principally by binary collisions (see p. 13).

Following the result of Landau and Teller given by (47), $Z_{10}$ has been plotted against $\sqrt{\bar{\nu} M}$ in Figure 21. A theoretical curve has been drawn to fit the data using $\gamma = 0.25 \AA$ and $\alpha = 0.5$. This value of $\gamma$ is about 1/8 the diameter of the colliding molecules and therefore is not reasonable. A similar curve drawn with $\gamma = 1 \AA$ will not fit the data regardless of the $\alpha$ used. Furthermore, the data do not appear to fit a single curve of the type drawn. It therefore appears that the theory of Landau and Teller does not fit the de-excitation of molecular vibrations in these gases.

In Figure 22 $Z_{10}$ has been plotted against $\bar{\nu}$ in accordance with (55) and the energy excitation theory.
Curves have been drawn using the values: $\omega = 1/12$, $n = 1.8, 1.5, 2.8$ and $3.8$. The value of $n$ to be used apparently depends upon the number of hydrogen atoms replaced from the methane molecule. The quantity $nh\gamma$ gives the minimum energy of approach necessary to excite or de-excite the vibrations of the molecule. This is presumably the energy necessary for the molecules to penetrate deeply into each other's force fields or to form a compound molecule as suggested on page 23.

Fogg, Hanks and Lambert (1953) have measured the relaxation times of some of the halogen-substituted methanes. Their values for $Z_{10}$ were computed from their relaxation data by making the assumption that $h\gamma \gg kT$ and hence that $Z_{10} \approx \rho \Theta$. At values of $\gamma < 500 \text{ cm}^{-1}$, this is not true and leads to error in $Z_{10}$ at low frequencies. In accordance with (40), their values for $Z_{10}$ have been multiplied by a factor $1 + e^{-h\gamma/kT}$. The values of $Z_{10}$ thus corrected, are recorded in Table III.

The above data were taken at temperatures of about 373 degrees Kelvin. The temperature correction predicted by (56) has been used to correct $Z_{10}$ to 300 degrees Kelvin; these values are also recorded in Table III. The corrections thus calculated, however, were invariably larger than the differences between these points and the calculated $Z_{10}$ curves. The values of $Z_{10}$ for 373 degrees Kelvin
<table>
<thead>
<tr>
<th>Gas</th>
<th>Investigator</th>
<th>T (°K)</th>
<th>$Q \times 10^8$ (sec)</th>
<th>$Z_{10}$</th>
<th>$Z_{10}$ (T=300°K) (cm$^{-1}$)</th>
<th>$\gamma_t$</th>
<th>$\gamma_{M_0 M_1}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I</td>
<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>4.5</td>
<td>86</td>
<td>176</td>
<td>533</td>
<td>342</td>
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<tr>
<td>CHCl$_3$</td>
<td>Fogg, Hanks, Lambert</td>
<td>383</td>
<td>2.8</td>
<td>83</td>
<td>139</td>
<td>260</td>
<td>200</td>
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<tr>
<td>CH$_2$Cl$_2$</td>
<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>8.4</td>
<td>204</td>
<td>466</td>
<td>283</td>
<td>192</td>
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<tr>
<td>CH$_3$F</td>
<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>320</td>
<td>6070</td>
<td>29400</td>
<td>1048</td>
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<tr>
<td>CCl$_4$</td>
<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>8.3</td>
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<td>348</td>
<td>218</td>
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<tr>
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<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>10</td>
<td>202</td>
<td>468</td>
<td>611</td>
<td>328</td>
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<tr>
<td>CH$_2$F$_2$</td>
<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>5.5</td>
<td>136</td>
<td>278</td>
<td>532</td>
<td>248</td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>Fogg, Hanks, Lambert</td>
<td>373</td>
<td>42</td>
<td>1200</td>
<td>3720</td>
<td>508</td>
<td>263</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>Fogg, Hanks, Lambert Griffith</td>
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<td>18</td>
<td>424</td>
<td>1200</td>
<td>732</td>
<td>300</td>
</tr>
<tr>
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<td>Fogg, Hanks, Lambert Griffith</td>
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<td>20.2</td>
<td>956</td>
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<td>956</td>
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<td>CF$_4$</td>
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<tr>
<td>CH$_4$</td>
<td>Sucken and Aybar</td>
<td>382</td>
<td>84</td>
<td>6000</td>
<td>36000</td>
<td>1306</td>
<td>302</td>
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<tr>
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<td>Huber and Zantrowitz Griffith</td>
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<td>2</td>
<td>49</td>
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<td>260</td>
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</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>Griffith</td>
<td>292</td>
<td>8</td>
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</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>Griffith</td>
<td>294</td>
<td>10</td>
<td></td>
<td></td>
<td>369</td>
<td>227</td>
</tr>
</tbody>
</table>
and also the values predicted for 300 degrees Kelvin are shown in Figure 22.

Several other authors have measured relaxation times in some of the halogen-substituted methanes. Byers (1943), Euoken and Aybar (1940) and Petralia (1952) have used acoustio interferometers to measure relaxation times; Griffith (1950) and Huber and Kantrowitz (1947) have made measurements using Kantrowitz-type impact nozzles. Their data are also reported in Table III, and the corresponding values of $Z_{10}$ are plotted in Figure 22. Where the measurements were made at temperatures more than a few degrees removed from 300 degrees Kelvin, the data are corrected to this temperature by use of (56).

The fact that use of (56) gives too large temperature corrections might suggest that the steric factor $\alpha$ is a function of temperature. It is reasonable to assume that $\alpha$, being a geometrical probability, is dependent upon the speed at which the molecules are rotating, which in turn is a function of temperature. The period of a rotation of a typical molecule is $10^{-12}$ second which is of the same order as the duration of a molecular collision.
Figure 1. Sonic velocity and absorption for thermal relaxation process

\[
\omega_{\text{inf}} = \frac{C_0}{\theta C_\infty}
\]

\[
V_0^2 = \frac{RT}{M} \left( 1 + \frac{R}{C_\infty} \right)
\]

\[
\mu_{\text{max}} = \pi \left( \frac{V_\infty}{V_0} - \frac{V_0}{V_\infty} \right)
\]

\[
\omega_{\text{max}} = \frac{V_0 C_0}{\theta V_\infty C_\infty}
\]
Figure 2. Interferometer cup showing crystal mounting
Figure 3. The crystal oscillator circuit
Figure 4. Crystal impedance measuring circuit
Figure 5. Power supply with voltage regulator
Figure 6. Gas handling equipment
Figure 7. Velocity dispersion
$f/p$ in cycles per atmosphere

Frequency dispersion in $\text{CH}_3\text{Br}$
Figure 8. Velocity dispersion in CHClF.
in cycles per atmosphere

on in CHClF₂
Figure 9. Velocity dispers
in cycles per atmosphere

velocity dispersion in CH$_3$Cl
Figure 10. Velocity dispersion
cycles per atmosphere

city dispersion in CCl₃F
Figure II. Velocity dispersion
in cycles per atmosphere

Velocity dispersion in CBrClF₂
Figure 12. Velocity dis
Dispersions in $\text{CF}_4$
Figure 13. Velocity distribution

\[ V^2 \times 10^{-2} \text{ in (m/sec)}^2 \]

\[ f/p \text{ in cycle} \]

640
630
620
610
600
590
580
570

\[ 10^5 \]

\[ 10^6 \]
dispersion in CH$_2$F$_2$
Figure 14. Velocity dispersion

\[ V^2 \times 10^{-2} \text{ in} (\text{m/sec})^2 \]

vs.

\[ f/p \text{ in cycles} \]

\( \times 10^5 \) to \( \times 10^6 \)
city dispersion in CH₂ClF
$V^2 \times 10^{-2}$ in (m/sec)$^2$

Figure 15. Velocity
cycles per atmosphere

Velocity dispersion in CClF₃
Figure 16. Veloci
in cycles per atmosphere

Velocity dispersion in CHCl$_2$F
Figure 17. Velocity distribution

\[ V_x^2 \times 10^{-2} \text{ in (m/sec)}^2 \]
in cycles per atmosphere

Inf. pt.

Velocity dispersion in CHF$_3$
$V^2 \times 10^{-2}$ in (m/sec)$^2$

Figure 18. Velocity
cycles per atmosphere

velocity dispersion in CCl$_2$F$_2$
Figure 19. Velocity dispersion

$V^2 \times 10^{-2}$
in $(m/sec)^2$

$f/p$ in cycles $p$
p in cycles per atmosphere

Velocity dispersion in CBr$_2$F$_2$
Figure 20. Velocity dispersion diagram.
Velocity dispersion in CBrF$_3$
Figure 21. $Z_{10}$ interpreted by Landau–Teller theory
Figure 22. $Z_{10}$ interpreted by energy excitation
\( \alpha = 0.1 \quad n = 2.8 \)

\( \alpha = 0.1 \quad n = 1.8 \)

\( \alpha = 0.1 \quad n = 1.5 \)

1. CBr\(_2\)F\(_2\)
2. CBr\(_2\)Cl\(_2\)
3. CCl\(_4\)
4. CCl\(_3\)F
5. CCl\(_2\)F\(_2\)
6. CBrF\(_3\)
7. CClF\(_3\)
8. CF\(_4\)
9. CHCl\(_3\)
10. CHCl\(_2\)F
11. CHClF\(_2\)
12. CHF\(_3\)
13. CH\(_2\)ClF
14. CH\(_2\)Cl\(_2\)
15. CH\(_2\)F\(_2\)
16. CH\(_3\)I
17. CH\(_3\)Br
18. CH\(_3\)Cl
19. CH\(_3\)F
20. CH\(_4\)

\( \bar{\nu}, \text{ in cm}^{-1} \)

excitation theory
CONCLUSIONS

On the basis of the data reported in this dissertation, the following conclusions may be drawn:

1. Intermodal coupling is so strong in the halogen-substituted methanes that once the vibrational mode of lowest frequency is excited, the energy passes readily into the other modes.

2. Only binary collisions are important in the excitation of vibrations in the halogen-substituted methanes within the limits of observation.

3. The probability, in a given collision, of exciting or de-exciting molecular vibrations in the halogen-substituted methanes appears to depend upon the relative energy of approach of the colliding molecules rather than upon their relative velocity as the Landau-Teller Theory predicts. In particular, the probability of excitation or de-excitation is negligible unless the relative energy of approach exceeds $E^* = n \hbar \nu_f$ where $n$ is characterized by the number of hydrogen atoms replaced. $\nu_f$ is the lowest vibrational frequency.

4. The excitation of vibrations in polyatomic organic molecules may be a complex process involving the formation of a compound molecule with a very short lifetime.

5. The steric factor probably depends upon temperature through its dependence upon rotational velocity.
LITERATURE CITED


Pierce, G. W. 1925. Piezoelectric crystal oscillators applied to the precision measurement of the velocity of sound in air and CO2 at high frequencies. Proc. Am. Acad. Arts and Sciences, 60: 271.


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