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A COMPARISON OF ROTATIONAL COLLISION NUMBERS OBTAINED FROM DIFFERENT DEFINITIONS

by Frank J. Zeleznik

Lewis Research Center
Cleveland, Ohio

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ABSTRACT

Two different definitions of rotational relaxation times were used to calculate rotational collision numbers for pure polar gases. One definition was based on the relaxation equation for rotational energy while the other was based on the connection between relaxation time and volume viscosity. For the purposes of the calculation, a polar molecule was taken to be a point dipole imbedded in a hard core and the interaction between molecules was confined to a plane. A classical calculation showed that the two definitions are equivalent, at least through the third order of a perturbation calculation. Both definitions predicted that increasing the temperature and decreasing the dipole moment and moment of inertia should increase the rotational collision number. The results are in qualitative agreement with experiment insofar as the dipole moment and moment of inertia dependence are concerned. No conclusion can be made concerning the correctness of the theoretical temperature dependence since the experimental temperature dependence is somewhat in doubt.

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SUMMARY

Two different definitions of rotational relaxation times were used to calculate rotational collision numbers for pure polar gases. One definition was based on the relaxation equation for rotational energy while the other was based on the connection between relaxation time and volume viscosity. For the purposes of the calculation, a polar molecule was taken to be a point dipole imbedded in a hard core and the interaction between molecules was confined to a plane. A classical calculation showed that the two definitions are equivalent, at least through the third order of a perturbation calculation. Both definitions predicted that increasing the temperature and decreasing the dipole moment and moment of inertia should increase the rotational collision number. The results are in qualitative agreement with experiment insofar as the dipole moment and moment of inertia dependence are concerned. No conclusion can be made concerning the correctness of the theoretical temperature dependence since the experimental temperature dependence is somewhat in doubt.

INTRODUCTION

In comparison with vibrational relaxation, relatively little experimental data on rotational relaxation exist in the literature. This is particularly true of rotational relaxation in polar gases, and, until quite recently, experimental values have been almost nonexistent. However, recent experimental studies have yielded rotational relaxation times, or equivalently, rotational collision numbers for a number of the more common polar gases (refs. 1 to 10). Some of the available data is summarized in table I. The data (ref. 9) for the molecule NO have not been included because it is considerably less polar than the molecules of table I, and hence the dipole-dipole potential is probably not the dominant interaction. In addition, a Z_{ROT} for ammonia, determined by Petralia (ref. 11), has not been included since it is approximately four times larger than the corresponding value in table I. In a private communication, Dr. R. S. Brokaw of this laboratory expressed the opinion that the Z_{ROT} for H_2S that is given in table I appears unrealistically large when compared with similar molecules. However, I have included it in the tabulation because it is the only data available for this molecule. Except for the fluoromethanes, the experimental collision numbers have been obtained from an analysis of either acoustic absorption or thermal conductivity measurements. The fluoromethane data were derived from nuclear magnetic resonance spectra (ref. 10). It is by no means certain that the three experimental techniques give comparable values for the rotational collision number Z_{ROT}. The two molecules HCl and H_2O can be used to compare the results from thermal conductivity and acoustic measurements. These two methods appear to give consistent results as is shown in figure 1. This agreement is quite important since thermal conductivity measurements coupled with the theory of Mason and Monchick (ref. 12) promises to be the most convenient way of obtaining Z_{ROT}. The NMR experiments also appear to give results that are comparable to those from thermal conductivity measurements, at least for spherically symmetric molecules (ref. 10).

There are three obvious parameters that could affect the rotational collision number of a polar gas: (1) the magnitude of the permanent electric dipole moment, (2) the mass

TABLE I. - PROPERTIES OF POLAR GASES

(a) Molecular properties

Molecule	Electric dipole moment, μ, (esu)(cm^2)	Molecular weight, M	Moments of inertia, (g-cm^2)			Average moment of inertia, I	Moment of inertia to molecular weight ratio, I/M
			I_A	I_B	I_C		
HCl	1.081×10^{-18}	36.469	-------------	2.6431×10^{-40}	--------------	2.6431×10^{-40}	0.725×10^{-41}
DCl	1.085	37.476	-------------	5.1404	--------------	5.1404	1.372
HF	1.83	20.008	-------------	1.33563	--------------	1.33563	.668
DF	1.837	21.014	-------------	2.54140	--------------	2.54140	1.209
H_2O	1.844	18.016	1.0224×10^{-40}	1.9180	2.9404×10^{-40}	1.9603	1.088
D_2O	1.861	20.029	1.833	3.841	5.674	3.7827	1.889
NH_3	1.477	17.032	4.4140	2.8087	2.8087	3.3438	1.963
ND_3	1.509	20.050	8.7960	5.4129	5.4129	6.5406	3.262
$^{15}NH_3$	1.477	18.033	4.4140	2.8159	2.8159	3.3486	1.857
SO_2	1.631	64.063	95.351	81.322	13.806	63.493	.991
CHF_3	1.645	70.019	81.08	81.08	148.67	103.61	14.797
CH_2F_2	1.93	52.026	17.1	79.1	90.7	62.3	11.975
CH_3F	1.85	34.034	5.52	32.854	32.854	23.74	6.975
H_2S	.92	34.080	5.8008	3.1020	2.7040	3.8693	1.135

TABLE I. - Concluded. PROPERTIES OF POLAR GASES

(b) Experimental rotational collision numbers

Molecule	Temperature, K	Rotational collision number, Z_{ROT}	Data from reference	Method (a)
HCl	273.2	7.0	8	A
	300.1	6.2	2	T
	328.5	4.6	↓	↓
	374.8	3.6		
	423.1	3.2		
	471.4	3.0		
DCl	300.1	2.6	2	T
	328.5	2.3	↓	↓
	374.8	2.0		
	423.1	1.9		
	471.4	1.9		
HF	373.75	9.5	3	T
	422.30	9.1	3	T
DF	373.75	4.1	3	T
	422.30	3.8	3	T
H_2O	323.2	4.0	7	A
	381.2	2.7	1	T
	426.1	2.5	↓	↓
	478.0	2.3		
	525.6	2.0		
D_2O	381.2	1.6	1	T
	426.1	1.5	↓	↓
	478.0	1.3		
	525.6	1.2		
NH_3	300.0	2.3	2	T
	329.1	2.1	↓	↓
	374.6	1.9		
	424.2	1.7		
	474.5	1.6		
	311.2	1.665	5	
	333.2	1.700	↓	
	353.2	1.709		
	373.2	1.866		
	393.2	2.000		
	413.2	2.073		
	433.2	2.144		
	453.2	2.299		
	473.2	2.628		
ND_3	300.0	1.6	2	T
	329.1	1.5	↓	↓
	374.6	1.3		
	424.2	1.3		
	474.5	1.2		
$^{15}NH_3$	300.0	2.5	2	T
	424.2	1.8	2	T
SO_2	300	1.2	4	T
	500	1.8	↓	↓
	700	3.3		
	900	6.9		
CHF_3	300	2.01	10	N
CH_2F_2	300	1.54	10	N
CH_3F	300	3.61	10	N
H_2S	298.2	31.2	6	A

[a] T, thermal conductivity; A, acoustic absorption; N, nuclear magnetic resonance.

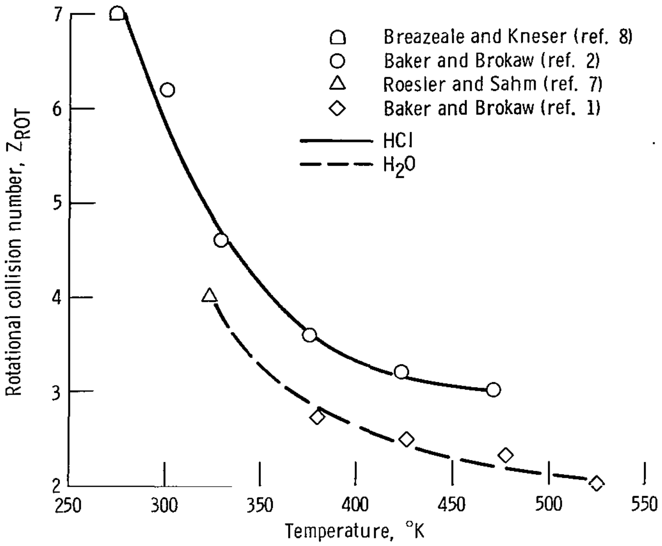

Figure 1. - Comparison of rotational collision number as obtained from acoustic absorption and thermal conductivity measurements.

distribution as characterized by the ratio of an arithmetic mean moment of inertia I to the mass M, and (3) the temperature T. The qualitative effect of these parameters can be deduced from the values of Z_{ROT} and the molecular properties that are given in table I. Thus, the pair of molecules H_2O and H_2S have approximately the same value of I/M but appreciably different dipole moments; a similar relation exists between the pair D_2O and $^{15}NH_3$. The data for these two pairs of molecules indicate that an increase in the dipole moment produces a decrease in Z_{ROT}. This effect was first noted by Brezeale and Kneser (ref. 8) when they compared the Z_{ROT} for HCl with that of similar nonpolar molecules. To determine the role of mass distribution in the rotational relaxation process, we can compare the pair of molecules HCl and DCl since they have very nearly the same dipole moments. This is also true of the pair H_2O and D_2O and the set of molecules NH_3, $^{15}NH_3$, and ND_3. These comparisons indicate that an increase in I/M produces a decrease in Z_{ROT}. Finally, the data of table I can be examined to determine the temperature dependence of Z_{ROT}. All the molecules, with the exception of SO_2 and NH_3, have a Z_{ROT} that decreases with temperature. The Z_{ROT} for SO_2 increases with temperature. For NH_3, the experiments of Baker and Brokaw (ref. 2) gave a Z_{ROT} that decreases with temperature, but the similar experiments of Srivastava and Das Gupta (ref. 5) showed the opposite results. It is interesting to note that only a small change (2 to 3 percent) in the thermal conductivity values of Srivastava and Das Gupta is sufficient to make Z_{ROT} a decreasing function of temperature (ref. 5). This sensitivity makes the temperature dependence of Z_{ROT} uncertain.

The experimentally deduced effects of the parameters I/M and T cannot be compared with theoretical predictions since no theoretical calculations of Z_{ROT} for polar gases exist. However, some classical calculations have been made for a number of nonpolar gas models. Sather and Dahler (refs. 13 and 14) have examined the rough sphere, the spherocylinder, and the loaded sphere gas molecules. For the rough sphere the find

$$Z_{ROT}^{-1} \propto (4I/M\sigma^2)\Big/\left(1 + 4I/M\sigma^2\right)^2$$

where I is the moment of the inertia, M the molecular mass, and σ the molecular diameter. Because $4I/M\sigma^2 << 1$, the Z_{ROT} decreases with increasing I/M. For the spherocylinder and the loaded sphere, their calculations show the opposite dependence, that is, Z_{ROT} increases with increase in I/M. Widom's calculations (ref. 15) for rough sphere molecules being relaxed by an inert gas give a dependence on I/M similar to Sather and Dahler's rough sphere results. Using a somewhat more realistic potential but restricting collisions to a plane, Parker (ref. 16) showed that the rotational collision number increased linearly with I/M. Finally, Brout's (refs. 17 and 18) quantum mechanical calculations imply a decreasing Z_{ROT} with increasing I/M. The theoretical temperature dependence of Z_{ROT}, like its mass distribution dependence, is a strong function of the model used in the calculation. For rough spheres, spherocylinders and loaded spheres, Sather and Dahler (refs. 13 and 14) find Z_{ROT} to be independent of temperature. However, when the rough spheres and the spherocylinders are surrounded by a square well potential, the rotational collision number becomes a rapidly increasing function of temperature. Parker (ref. 16) also obtained a Z_{ROT} that increases with temperature although at a somewhat greater rate than the square-well models.

Recently Nyeland (ref. 19) reapplied Parker's model for the calculation of Z_{ROT} but used a different definition for Z_{ROT}; the two possible definitions are discussed in the next section. In contrast to Parker's results, Nyeland's Z_{ROT} decreased with an increase in the moment of inertia and had a smaller rate of increase with temperature. This difference might be due either to the use of different definitions or to different approximations in the calculation.

In view of the present uncertainties concerning the rotational relaxation of polar gases, it seemed desirable to attempt a theoretical treatment of the problem. It would be preferable to carry out a quantum mechanical treatment, and, indeed, Cross and Gordon (ref. 20) have recently evaluated the first Born approximation to the scattering matrix for scattering from point dipoles. However, they make no attempt to account for short range interactions since their primary concern is with the effect of resonant scattering on the total scattering cross section. It has been conjectured by Mason and Monchick (ref. 12) that resonant scattering is also a significant effect in rotational relaxation. However, based on experimental results, Baker and Brokaw (ref. 1) suggest that the effect may be classical rather than quantum mechanical. For this reason, it would be desirable to see what extent classical mechanics can account for the experimental observations. An additional objective is to ascertain the effect of using different definitions of relaxation times.

The calculation I shall describe is essentially a classical perturbation calculation of the change in rotational energy produced by the scattering of permanent electric dipoles. The molecules are constrained to a plane and no out-of-plane forces are permitted. This sacrifice of some of the physical reality is necessary in order to make the calculation mathematically tractable. The calculation is by no means trivial even with this assumption. The interaction potential and the details of the computation differ considerably from Parker's, although both are two dimensional. I shall employ an interaction picture of classical mechanics as described by Garrido (refs. 21 and 22). For convenience, pertinent features of Garrido's method are summarized in appendix A.

ROTATIONAL RELAXATION TIMES

Two definitions of relaxation times have appeared in the literature. These two definitions have not been shown to be equal; however, they are often used interchangeably. The first of these definitions is a phenomenological one and corresponds to the ad hoc introduction of an additional equation (and an adjustable parameter) to supplement the usual hydrodynamic-thermodynamic equations of continuum mechanics. This supplementary equation was initially introduced to explain acoustic absorption experiments. The new parameter, known as a relaxation time, is defined by the supplementary equation. If we restrict our attention to rotational energy, then the rotational relaxation time τ_R is defined by

$$\frac{dE_R}{dt} = \frac{E_R(T) - E_R(t)}{\tau_R} \tag{1}$$

In this equation E_R is the contribution of rotational energy to the thermodynamic internal energy. The equilibrium value of the rotational internal energy is $E_R(T)$ while the instantaneous, nonequilibrium value is $E_R(t)$.

The alternate definition of a relaxation time is based on the fact that at low acoustic frequencies it is impossible to experimentally separate the absorption of acoustic energy due to viscous-thermal effects from that due to a relaxation phenomena (ref. 23). The absorption can be corrected for the effects of shear viscosity and thermal conductivity using experimentally determined values of shear viscosity and thermal conductivity. It cannot, however, be corrected for the absorption due to volume (or bulk) viscosity since there is no known experiment that independently measures this transport coefficient. Consequently, little is known about the volume viscosity and it has become common practice to equate the volume viscosity absorption with the relaxation absorptions. This leads to a relaxation time, τ_R', defined in terms of the volume viscosity κ by the equation

$$(\tau_R')^{-1} = \nu kT \left(\frac{C_{int}}{C_v}\right)^2 \left(\frac{k}{C_{int}}\right) \kappa^{-1} \tag{2}$$

where ν is the number density of particles, C_v is the heat capacity at constant volume, and C_{int} is the contribution of internal motions to C_v. The contribution to C_{int} is only from rotational motion in our case. Equation (2) can be obtained by combining equations (38) and (74) of the paper by Wang Chang and Uhlenbeck (ref. 24). Wang Chang and Uhlenbeck have deduced an expression for κ by generating the normal solution of the Boltzmann equation and I shall use the classical equivalent of their semiclassical expression for κ in my calculation of τ_R'.

Rotational relaxation times, obtained from experiments are generally $O(10^{-10}$ sec). Therefore, it becomes convenient to express relaxation times on a different time scale. This time scale is determined by τ_c, defined to be the mean time between collisions and is a number $O(10^{-10}$ sec). Relaxation times expressed on this time scale are known as collision numbers Z. Since we have two rotational relaxation times, τ_R and τ_R', we also have two rotational relaxation collision numbers

$$\left.\begin{aligned} Z_{ROT} &= \frac{\tau_R}{\tau_c} \\ Z_{ROT}' &= \frac{\tau_R'}{\tau_c} \end{aligned}\right\} \tag{3}$$

In a later portion of this report we will show that the calculation of Z_{ROT} is essentially the calculation of the average change in rotational energy while the calculation of Z_{ROT}' reduces to the calculations of the average of the square of the rotational energy change. The following three sections of this report are devoted to this task.

Rotational Energy Change in a Collision

The change in rotational energy produced by a collision will be calculated for the two-dimensional model of molecules constrained to the x-y plane. The molecules will have a mass M_k, moment of inertia I_k about an axis perpendicular to the x-y plane, and a permanent electric dipole moment μ_k constrained to the x-y plane. The interaction will be the electric dipole-dipole interaction to which will be added a spherical hard core of diameter σ. The situation is depicted in figure 2, which also defines the coordinates of the problem in the center of mass coordinate system. The Hamiltonian for the model is a sum of four terms, the relative translational kinetic energy H_T, the rotational kinetic energy H_R, a spherically symmetric short range interaction Φ, and the dipole-dipole interaction potential V. Using upper case letters for the translational coordinates and momenta, and lower case letters for rotational coordinates and momenta, we can write

$$H = H_0 + V \tag{4}$$

where

$$H_0 = H_T + H_R + \Phi \tag{5}$$

For simplicity, Φ is taken to be a spherical hard core potential of diameter $\sigma = (\sigma_1 + \sigma_2)/2$ where σ_1 and σ_2 are the molecular diameters of the colliding molecules. The explicit expressions for H_T, H_R, and V are given in equations (6) to (8).

$$H_T = \frac{1}{2m}\left[(P_1)^2 + \left(\frac{P_2}{Q_1}\right)^2\right] \tag{6}$$

The coordinates Q_1 and Q_2 are the radius and angle of polar coordinates, while P_1 and P_2 are the conjugate momenta.

$$H_R = \frac{1}{2}\left[\frac{(p_1)^2}{I_1} + \frac{(p_2)^2}{I_2}\right] \tag{7}$$

$$V = \frac{\mu_1\mu_2}{(Q_1)^3}\left[\cos(q_1 - q_2) - 3\cos(q_1 - Q_2)\cos(q_2 - Q_2)\right] \tag{8}$$

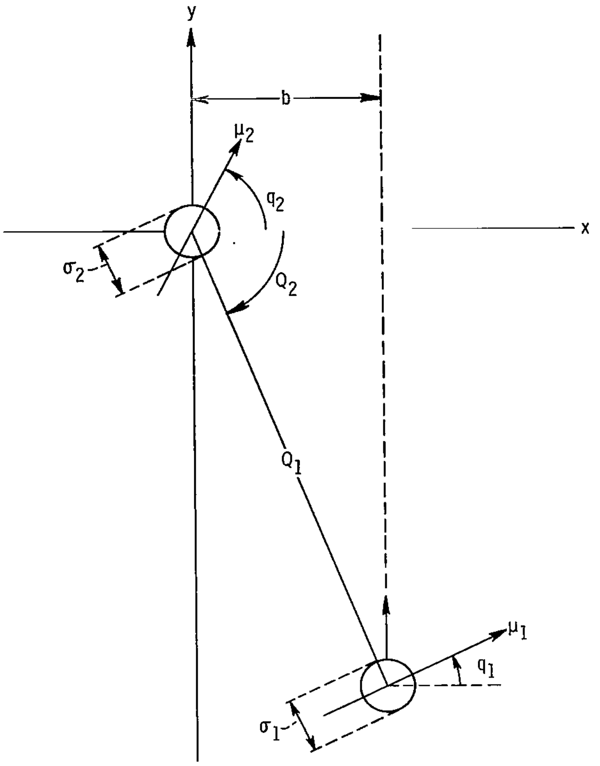

Figure 2. - Unperturbed trajectories for scattering of point dipoles with impact parameters greater than molecular diameter.

The coordinates q_1 and q_2 are angles specifying the orientation of the dipoles and p_1 and p_2 are the conjugate momenta. All angles are positive when measured counterclockwise and m is the reduced mass. The dipole-dipole interaction can be rewritten in the alternate form

$$V = -\frac{\mu_1\mu_2}{2(Q_1)^3}\left[\cos(q_1 - q_2) + 3\cos(q_1 + q_2 - 2Q_2)\right] \tag{9}$$

For the unperturbed problem, both H_T and H_R are constants of the motion

$$H_T^o = E \tag{10}$$

$$H_R^o = E_R \tag{11}$$

where E is the relative translational energy, and E_R the rotational energy. The rotational momenta are also constants of the motion for the unperturbed problem

$$p_k^o(t) = p_k^o(t') \tag{12}$$

while the rotational coordinates are given by

$$q_k^o(t) = q_k^o(t') + \frac{p_k^o(t')}{I_k}(t - t') \tag{13}$$

The unperturbed problem for the translation part is also easily solved; however, for the purpose of this paper, we only need the time dependence of Q_1 and Q_2. The time origin is taken at the point of closest approach on the unperturbed trajectory ($Q_2^o = 0$). For impact parameters $b \geq \sigma$ the incident particle is moving parallel to the y-axis and Q_1^o and Q_2^o satisfy

$$\left.\begin{aligned} \left[Q_1^o(t)\right]^2 &= \frac{2E}{m}t^2 + b^2 \\ \cos Q_2^o(t) &= \frac{b}{Q_1^o(t)} \qquad b \geq \sigma \\ \sin Q_2^o(t) &= \left(\frac{2E}{m}\right)^{1/2}\frac{t}{Q_1^o(t)} \end{aligned}\right\} \tag{14}$$

In equation (14), $2E/m$ is simply the square of the relative velocity. From these equations it is apparent that Q_1^o is an even function of t while Q_2^o is an odd function of t. For impact parameters $b < \sigma$, the unperturbed trajectories are again selected so that Q_1^o and Q_2^o have this same symmetry. This can be accomplished by a rotation of the coordinates x, y and the new situation is shown in figure 3. The Q_1^o and Q_2^o are described by the equations

$$\left.\begin{aligned}
\left[Q_1^o(t)\right]^2 &= \left[\left(\frac{2E}{m}\right)^{1/2} |t| + \sigma \cos \psi\right]^2 + \sigma^2 \sin^2 \psi \\
\cos Q_2^o(t) &= \frac{\left[\sigma + \left(\frac{2E}{m}\right)^{1/2} |t| \cos \psi\right]}{Q_1^o(t)} \qquad b < \sigma \\
\sin Q_2^o(t) &= \frac{\left(\frac{2E}{m}\right)^{1/2} |t| \sin \psi}{Q_1^o(t)}
\end{aligned}\right\} \qquad (15)$$

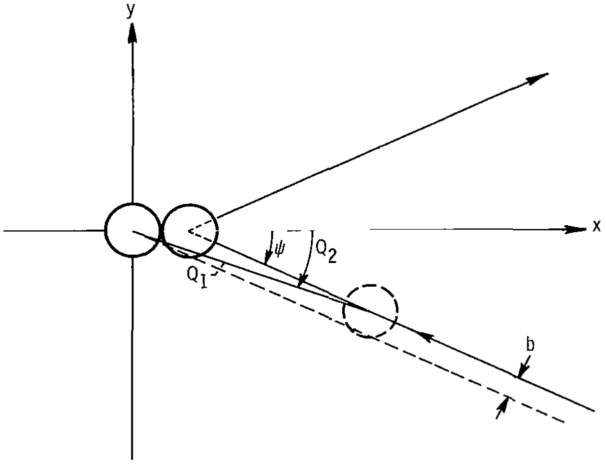

Figure 3. - Unperturbed trajectories for scattering of point dipoles with impact parameters less than molecular diameter.

In equation (15), the angle ψ is defined by

$$\sin \psi = \left(\frac{b}{\sigma}\right) \operatorname{sgn}(t) \qquad (16)$$

where sgn(t) represents the sign of the time variable.

The change in rotational energy, $\Delta E_R = H_R(t = +\infty) - H_R(t = -\infty)$, that occurs as a result of the scattering can be calculated from equations (A18) and (A19) of appendix A by using H_R as the dynamical variable F and by passing to the limit $t \to \infty$ and

$t_0 \to -\infty$. Since $H_R(t = -\infty) = H_R^o(t = -\infty)$ by virtue of choice of initial conditions and since H_R^o is a constant of the motion along the unperturbed trajectory, we have

$$\Delta E_R = H_R^{(1)} + H_R^{(2)} + \ldots = \sum_{n=1}^{\infty} H_R^{(n)} \tag{17}$$

where the first and second order terms are given by the integrals

$$\left.\begin{aligned} H_R^{(1)} &= \lim_{\substack{t \to \infty \\ t_0 \to -\infty}} \int_{t_0}^{t} dt'\, \Omega^1(t') H_R^o(t) \\ H_R^{(2)} &= \lim_{\substack{t \to \infty \\ t_0 \to -\infty}} \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, \Omega^1(t'')\Omega^1(t') H_R^o(t) \end{aligned}\right\} \tag{18}$$

The operator $\Omega^1(t)$ is the Poisson bracket operator containing V. The dynamical variable H_R contains only the rotational momenta P_k and not the translational momenta P_k. Therefore, it is only necessary to evaluate the effect of the operator $\Omega^1(t')$ on the P_k, and in turn, this requires the evaluation of the partial derivatives of equations (12) and (13) with respect to $p_j^o(t')$

$$\frac{\partial p_k^o(t)}{\partial p_j^o(t')} = \delta_{kj} \qquad \frac{\partial q_k^o(t)}{\partial p_j^o(t')} = \frac{(t - t')}{I_k}\, \delta_{kj} \tag{19}$$

and the partial derivatives of $H_R^o(t)$ with respect to $p_k^o(t)$

$$\frac{\partial H_R^o(t)}{\partial p_k^o(t)} = \frac{p_k^o(t)}{I_k} \qquad \frac{\partial^2 H_R^o(t)}{\partial p_j^o(t)\partial p_k^o(t)} = \frac{\delta_{kj}}{I_k} \tag{20}$$

In equations (19) and (20), δ_{kj} is the Kronecker delta.

The calculation of rotational collision numbers Z_{ROT} requires not ΔE_R but ΔE_R averaged over all possible initial conditions, or equivalently, averaged over all possible unperturbed trajectories. The unperturbed trajectories are determined by specifying the rotational momenta p_k^o, the rotational coordinates at $t = 0$, $q_k^o(0)$, the translational energy E, and the impact parameter b. For a given impact parameter, I shall use a Boltzmann type distribution function characterized by a translational temperature T and a rotational temperature T_R. The normalized distribution function f can be written

$$f\,dE\,dp_1^o\,dp_2^o\,dq_1^o(0)\,dq_2^o(0) = \frac{1}{\Gamma(s+1)}\left(\frac{E}{kT}\right)^s e^{-E/kT}\,d\left(\frac{E}{kT}\right)\frac{e^{-H_R^o/kT_R}}{2\pi kT_R\sqrt{I_1 I_2}}\,dp_1^o\,dp_2^o\,\frac{dq_1^o(0)}{2\pi}\,\frac{dq_2^o(0)}{2\pi}$$

$$0 \le E \le \infty \qquad -\infty \le p_k^o \le \infty \qquad -\pi \le q_k^o(0) \le \pi \tag{21}$$

The choice of the parameter s determines the type of distribution function, and it can be used to introduce an element of three-dimensionality into the calculation. Thus, $s = 0$ corresponds to a two-dimensional Maxwell-Boltzmann distribution; $s = 1/2$ can be regarded as either a three-dimensional Maxwell-Boltzmann energy distribution or a two-dimensional flux distribution; and the value $s = 1$ corresponds to a three-dimensional flux distribution. The distribution function (21) can be written in a slightly more convenient form with the transformation

$$\lambda^{(\pm)} = \frac{1}{2}\left(\frac{p_1^o}{\sqrt{I_1}} \pm \frac{p_2^o}{\sqrt{I_2}}\right) \tag{22}$$

In terms of $\lambda^{(\pm)}$ the two-temperature distribution function takes the form

$$f\,dE\,d\lambda^{(+)}\,d\lambda^{(-)}\,dq_1^o(0)\,dq_2^o(0) = \frac{1}{\Gamma(s+1)}\left(\frac{E}{kT}\right)^s e^{-E/kT}\,d\left(\frac{E}{kT}\right)$$

$$\times\frac{\exp\left\{-\frac{\left[\lambda^{(+)^2}+\lambda^{(-)^2}\right]}{kT_R}\right\}}{\pi kT_R}\,d\lambda^{(+)}\,d\lambda^{(-)}\,\frac{dq_1^o(0)}{2\pi}\,\frac{dq_2^o(0)}{2\pi} \tag{23}$$

The distribution function, in the form (23), will be used to average (17). When ΔE_R is averaged over the dipole orientation $q_1^o(0)$ and $q_2^{(o)}(0)$, all odd order terms in the expression (17) disappear. This is most easily shown by noting that the n^{th} order term will always contain a factor of the form

$$G_{kl} = \int_{-\pi}^{\pi} \cos^k q_1^o(0)\, dq_1^o(0) \int_{-\pi}^{\pi} \sin^l q_2^o(0)\, dq_2^o(0) \qquad k + l = n$$

For the odd order terms, either k or l must be odd. But the result is always zero when an odd power of a trigonometric function is integrated over its period. Thus, if $\langle \Delta E_R \rangle$ denotes the average of ΔE_R over the distribution function (23), we have

$$\langle \Delta E_R \rangle = \left\langle H_R^{(2)} \right\rangle + \left\langle H_R^{(4)} \right\rangle + \ldots \tag{24}$$

The calculation of the rotational collision number Z'_{ROT} requires the calculation of $\langle (\Delta E_R)^2 \rangle$. The quantity $(\Delta E_R)^2$ can be expressed in terms of the perturbation expansion (17) to give the equation

$$\langle (\Delta E_R)^2 \rangle = \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \left\langle H_R^{(k)} H_R^{(l)} \right\rangle \tag{25}$$

In this equation, as well as the equation for $\langle \Delta E_R \rangle$, all odd order terms vanish. Thus we get an expression for $\langle (\Delta E_R)^2 \rangle$, that is analogous to (24).

$$\langle (\Delta E_R)^2 \rangle = \left\langle (H_R^{(1)})^2 \right\rangle + \left\langle (H_R^{(2)})^2 + 2H_R^{(1)} H_R^{(3)} \right\rangle + \ldots \tag{26}$$

If the first nonvanishing terms in (24) and (26) can be calculated, then we will have results that are valid through third order in perturbation theory for both Z_{ROT} and Z'_{ROT}. With these results we will be able to make a meaningful comparison of Z_{ROT} and Z'_{ROT}. That is, at least through third order in perturbation, we shall be able to make some conclusions regarding the equivalence or inequivalence of the two definitions of relaxation times τ_R, and τ'_R. The next section will describe the calculation of $\left\langle H_R^{(2)} \right\rangle$ while the following section will give the details in the calculation of $\left\langle (H_R^{(1)})^2 \right\rangle$.

Evaluation of Second Order Term $\left\langle H_R^{(2)} \right\rangle$

The integrand of $H_R^{(2)}$ can be evaluated by the application of equations (20) and (A21). This gives the result

$$\Omega^1(t'')\Omega^1(t')H_R^o(t) = \sum_k \frac{1}{I_k}\left[p_k^o(t)\Omega^1(t'')\Omega^1(t')p_k^o(t) + \Omega^1(t'')p_k^o(t)\Omega^1(t')p_k^o(t)\right] \tag{27}$$

It should be noted that the translational momenta P_k do not appear in (27) because H_R is only a function of the rotational momenta P_k. Furthermore, since the p_k^o and P_k^o are independent, (A22), when combined with equation (19), gives

$$\Omega^1(t')p_k^o(t) = -\frac{\partial V(t')}{\partial q_k^o(t')} \tag{28}$$

Operating on equation (28) with $\Omega^1(t'')$ (or by using (A23) and remembering that the second partial derivatives of p_k^o vanish) gives the expression

$$\Omega^1(t'')\Omega^1(t')p_k^o(t) = \sum_j \frac{\partial V(t'')}{\partial q_j^o(t'')}\,\frac{\partial^2 V(t')}{\partial q_j^o(t')\partial q_k^o(t')}\,\frac{(t' - t'')}{I_j} \tag{29}$$

Combining equations (28) and (29) with (27) and performing some rearrangements produces

$$\Omega^1(t'')\Omega^1(t')H_R^o(t) = \sum_k \frac{1}{I_k}\,\frac{\partial V(t'')}{\partial q_k^o(t'')}\left[\frac{\partial V(t')}{\partial q_k^o(t')} + (t' - t'')\sum_j \frac{p_j^o}{I_j}\,\frac{\partial^2 V(t')}{\partial q_j^o(t')\partial q_k^o(t')}\right] \tag{30}$$

where the time label on p_j^o has been suppressed since p_j^o is a constant along the unperturbed trajectories.

Upon evaluating the partial derivatives of the dipole-dipole interaction potential, using the form (9), and averaging equation (30) over the orientations $q_1^o(0)$ and $q_2^o(0)$, there results the relatively simple expression

$$\mathscr{H}(\omega^{(\pm)},E,b,t,t') \equiv \frac{1}{(2\pi)^2}\int_{-\pi}^{\pi} dq_1^o(0)\int_{-\pi}^{\pi} dq_2^o(0)\,\Omega^1(t'')\Omega^1(t')H_R^o(t) = \left[\frac{\mu_1^2\mu_2^2 I^{(+)}}{8I_1I_2}\right]$$

$$\times\frac{\left\{\cos\left[\omega^{(-)}(t'' - t')\right] + 9\cos\left[\omega^{(+)}(t'' - t') - 2Q_2^o(t'') + 2Q_2^o(t')\right] - \omega^{(-)}(t'' - t')\sin\left[\omega^{(-)}(t'' - t')\right] - 9\omega^{(+)}(t'' - t')\sin\left[\omega^{(+)}(t'' - t') - 2Q_2^o(t'') + 2Q_2^o(t')\right]\right\}}{\left[Q_1^o(t'')Q_2^o(t')\right]^3} \tag{31}$$

In this equation, I have used the notation

$$\omega^{(\pm)} = p_1^o/I_1 \pm p_2^o/I_2 \tag{32}$$

$$I^{(\pm)} = I_1 \pm I_2 \tag{33}$$

Equation (31) can be written in a somewhat more convenient form by introducing a parameter ϵ that will eventually be set equal to unity. Observing that

$$(1 + \partial/\partial\epsilon) \cos \epsilon\omega t \Big|_{\epsilon=1} = \cos \omega t - \omega t \sin \omega t \tag{34}$$

we can define a function $\mathscr{H}(\epsilon)$ as

$$\mathscr{H}(\epsilon) = \left[\frac{\mu_1^2\mu_2^2 I^{(+)}}{8I_1I_2}\right](1 + \partial/\partial\epsilon) \times \frac{\cos\left[\epsilon\omega^{(-)}(t'' - t')\right] + 9 \cos\left[\epsilon\omega^{(+)}(t'' - t') - 2Q_2^o(t'') + 2Q_2^o(t')\right]}{\left[Q_1^o(t'')Q_1^o(t')\right]^3} \tag{35}$$

such that $\mathscr{H}(1) = \mathscr{H}$. The integration of $\mathscr{H}(\epsilon)$ over the rotational energy distribution can be performed by using the relation between $\omega^{(\pm)}$ and $\lambda^{(\pm)}$

$$\omega^{(\pm)} = \pm \left(1/\sqrt{I_2} \pm 1/\sqrt{I_1}\right)\lambda^{(+)} \mp \left(1/\sqrt{I_2} \mp 1/\sqrt{I_1}\right)\lambda^{(-)} \tag{36}$$

to obtain the result

$$\frac{1}{\pi k T_R} \int_{-\infty}^{\infty} d\lambda^{(+)} \int_{-\infty}^{\infty} d\lambda^{(-)}\, \mathscr{H}(\epsilon) \exp\left[-\frac{\left(\lambda^{(+)2} + \lambda^{(-)2}\right)}{kT_R}\right] =$$

$$\left(\frac{\mu_1^2\mu_2^2 I^{(+)}}{8I_1I_2}\right)(1 + \partial/\partial\epsilon)\left\{1 + 9 \cos 2\left[Q_2(t') - Q_2(t'')\right]\right\} \frac{\exp\left[\dfrac{-\epsilon^2(t'' - t')^2 I^{(+)} kT_R}{2I_1I_2}\right]}{Q_1^o(t'')Q_1^o(t')^{\;3}} \tag{37}$$

To complete the evaluation of the second order term $\left\langle H_R^{(2)} \right\rangle$ it is still necessary to integrate equation (37) over the translational energy distribution and to perform integrations over t' and t'' between the limits given in (18). The integration limits for both time variables can be extended from $-\infty$ to $+\infty$, and the result multiplied by 1/2, because of the symmetry of equation (37) in t' and t''. This then allows $\left\langle H_R^{(2)} \right\rangle$ to be written as

$$\left\langle H_R^{(2)} \right\rangle = \lim_{\epsilon \to 1} \left(\frac{\mu_1^2 \mu_2^2}{4\sigma^6 kT} \right) \left(\frac{T}{T_R} \right) (1 + \partial/\partial\epsilon) \left[5A(\epsilon) - 9B(\epsilon) \right] \tag{38}$$

where the dimensionless functions $A(\epsilon)$ and $B(\epsilon)$ are defined by

$$A(\epsilon) = \frac{\sigma^6}{\tau_1^2 \Gamma(s+1)} \int_0^\infty dx\, x^s e^{-x} \iint_{-\infty}^{\infty} dt'\, dt''\, \frac{e^{-\epsilon^2 (t'' - t')^2 / \tau_1^2}}{\left[Q_1^0(t') Q_1^0(t'') \right]^3} \tag{39}$$

$$B(\epsilon) = \frac{\sigma^6}{\tau_1^2 \Gamma(s+1)} \int_0^\infty dx\, x^s e^{-x} \iint_{-\infty}^{\infty} dt'\, dt''\, \frac{\sin^2 \left[Q_2^0(t') - Q_2^0(t'') \right]}{\left[Q_1^0(t') Q_2^0(t'') \right]^3} e^{-\epsilon^2 (t'' - t')^2 / \tau_1^2} \tag{40}$$

In equations (39) and (40), $x = E/kT$ and the time scaling parameter τ_1 is defined by the expression

$$\tau_1^2 = \frac{2 I_1 I_2}{I^{(+)} k T_R} \tag{41}$$

Based on the equations for the unperturbed trajectories (14) and (15), two other time scales can be introduced by the definition

$$\tau^2 = \frac{m\sigma^2}{2E} = \frac{\tau_2^2}{x} \tag{42}$$

where

$$\tau_2^2 = \frac{m\sigma^2}{2kT} \tag{43}$$

The evaluation of the remaining integrals (39) and (40) is considerably simplified by the use of the Fourier transform. This is discussed in appendix B and the principal result is given as equation (B9). Combining equation (B9) with equation (38) gives $\left\langle H_R^{(2)} \right\rangle$ the form

$$\left\langle H_R^{(2)} \right\rangle = \lim_{\epsilon \to 1} \frac{\pi^{1/2}\Gamma(s+1/2)}{\Gamma(s+1)} \frac{\mu_1^2\mu_2^2}{\sigma^6 kT} \left(\frac{T}{T_R}\right)\left(\frac{\tau_2}{\tau_1}\right)(1 + \partial/\partial\epsilon) \int_0^\infty d\kappa \frac{\left(\frac{\tau_1}{2\epsilon\tau_2}\right)\rho(\kappa)}{\left[1 + \left(\frac{\kappa\tau_1}{2\epsilon\tau_2}\right)^2\right]^{s+1/2}} \tag{44}$$

Note that in equation (44) κ is merely used as an integration variable and is not the volume viscosity. This is true for the balance of this section and also in the following section. The actual form of the density function $\rho(\kappa)$ can be obtained by evaluating the appropriate Fourier sine and cosine transforms. By performing the indicated operations on the parameter ϵ, equation (44) becomes

$$\left\langle H_R^{(2)} \right\rangle = \frac{\pi^{1/2}\Gamma(s+3/2)}{2\Gamma(s+1)} \frac{\mu_1^2\mu_2^2}{\sigma^6 kT} \left(\frac{T}{T_R}\right) \int_0^\infty d\kappa \frac{\rho(\kappa)\kappa^2\zeta}{\left[1 + \kappa^2\zeta^2\right]^{s+3/2}} \tag{45}$$

where

$$\zeta^2 = \frac{\tau_1^2}{4\tau_2^2} = \left(\frac{I_1I_2}{I^{(+)}m\sigma^2}\right)\left(\frac{T}{T_R}\right) \tag{46}$$

The density function $\rho(\kappa)$ depends parametrically only on b/σ. The effect of the other parameters is given explicitly in equation (45). By using the letters C and S for the Fourier cosine and sine transforms, respectively, it becomes possible to write the density function $\rho(\kappa)$ in the form

$$\rho(\kappa) = 5C^2\left(\frac{\sigma^3}{Q_1^3}\right) - 18\left\{C\left[\left(\frac{\sigma}{Q_1}\right)^3 \sin^2 Q_2\right] C\left[\left(\frac{\sigma}{Q_1}\right)^3 \cos^2 Q_2\right] - S^2\left[\left(\frac{\sigma}{Q_1}\right)^3 \sin Q_2 \cos Q_2\right]\right\} \tag{47}$$

This expression can be evaluated analytically for $b/\sigma \geq 1$, that is, when Q_1 and Q_2 are given by equation (14); however, for $b/\sigma < 1$, $\rho(\kappa)$ must be calculated numerically. In the former case ($b/\sigma \geq 1$) all transforms are reducible to a form that can be recognized as either an integral representation of the modified Bessel functions of the second kind K_ν or a derivative of K_ν. The integral representation of K_ν is (ref. 25)

$$\sqrt{\frac{2}{\pi}} \int_0^\infty dz \frac{\cos \kappa z}{\left(z^2 + b^2/\sigma^2\right)^{\nu+1/2}} = \frac{2^{1/2}}{\Gamma(\nu + 1/2)} \left(\frac{\kappa\sigma}{2b}\right)^\nu K_\nu\left(\frac{\kappa b}{\sigma}\right) \tag{48}$$

by using equation (48), $\rho(\kappa)$ can be written as

$$\rho(\kappa) = \left(\frac{2}{\pi}\right)\left(\frac{\sigma}{b}\right)^4 \left[\left(5 + 2z^2\right)z^2K_1^2(z) - 6z^3K_1(z)K_2(z) + 2z^4K_2^2(z)\right] \qquad \frac{b}{\sigma} \geq 1 \tag{49}$$

where $z = \kappa b/\sigma$. This density function is finite everywhere and essentially goes to zero exponentially for large values of κ. For impact parameters less than σ the Fourier transforms that appear in equation (47) were evaluated numerically by the method devised by Longman (refs. 26 and 27). The function $\rho(\kappa)$ is shown in figure 4 for several values of b/σ. The value $\rho(0)$ can be calculated from

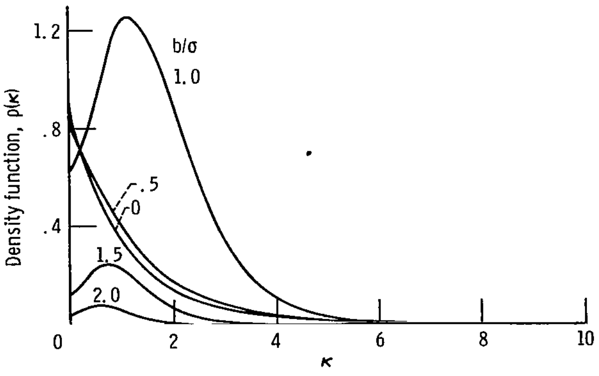

Figure 4. - Density function for rotational-translational energy transfer.

$$\rho(0) = \begin{cases} \left(\dfrac{2}{\pi}\right) \dfrac{1 + 9\Delta + \Delta^2 - \Delta^3}{(1 + \Delta)^3} & \dfrac{b}{\sigma} \leq 1 \\ \left(\dfrac{2}{\pi}\right)\left(\dfrac{\sigma}{b}\right)^4 & \dfrac{b}{\sigma} \geq 1 \end{cases} \tag{50}$$

where $\Delta^2 = 1 - (b/\sigma)^2$. The function $\kappa^2 \rho(\kappa)$ is plotted in figure 5 for several values of b/σ.

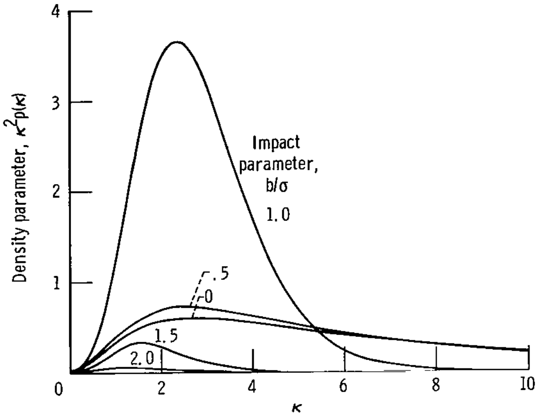

Figure 5. - Density function times κ^2.

Two integrations still remain undone. One of these is the average over impact parameters and the other is the integration indicated in equation (45). Equation (45) can be evaluated analytically for impact parameters greater than σ while for impact parameters less than σ it must be calculated numerically. Designating the integral in equation (45) by $\mathcal{E}_s$, changing the integration variable to $z = \kappa b/\sigma$, and substituting equation (49) for $\rho(\kappa)$ gives

$$\mathcal{E}_s \equiv \int_0^\infty d\kappa \frac{\rho(\kappa)\kappa^2\zeta}{(1 + \kappa^2\zeta^2)^{s+3/2}} = \left(\frac{2}{\pi}\right)\left(\frac{\sigma}{b}\right)^7 \zeta$$

$$\times \int_0^\infty dz \frac{z^2\left[(5 + 2z^2)z^2K_1^2(z) - 6z^3K_1(z)K_2(z) + 2z^4K_1^2(z)\right]}{\left[1 + \left(\zeta \dfrac{\sigma}{b}\right)^2 z^2\right]^{s+3/2}} \tag{51}$$

This integral can be evaluated by proceeding in a somewhat indirect fashion. The denominator is replaced by its Gaussian representation (ref. 28) by using

$$\frac{1}{r^\lambda} = \frac{1}{\Gamma\left(\frac{\lambda}{2}\right)} \int_0^\infty d\alpha\ \alpha^{\lambda/2-1}\ e^{-\alpha r^2}$$

This permits equation (51) to be written as

$$\mathscr{E}_s = \frac{2}{\pi}\left(\frac{\sigma}{b}\right)^7 \frac{\zeta}{\Gamma_{(s+3/2)}} \int_0^\infty d\alpha\ \alpha^{s+1/2}\ e^{-\alpha} \int_0^\infty dz\ e^{-\alpha(\zeta\sigma/b)^2 z^2}$$

$$\times\ z^2\left[(5 + 2z^2)z^2K_1^2(z) - 6z^3K_1(z)K_2(z) + 2z^4K_2^2(z)\right] \qquad (52)$$

The integration over z is of the type studied by Ragab (ref. 29) and can be expressed in terms of MacRobert's E function (ref. 30)

$$\int_0^\infty dz\ z^{l-1}K_m(z)K_n(z)e^{-z^2/\beta}$$

$$= \frac{\pi^{1/2}}{4} E\left(\frac{l+m+n}{2}, \frac{l+m-n}{2}, \frac{l-m+n}{2}, \frac{l-m-n}{2}: \frac{l}{2}, \frac{l+1}{2}: \beta\right) R_e(\beta) > 0,\ R_e(l \pm m \pm n) > 0$$

By using this result, the remaining integral over α is essentially the Laplace transform of MacRobert's E function. Transforms of this type were evaluated by Ragab (ref. 31) and have been tabulated by Erdelyi (ref. 32). Ragab showed that

$$\int_0^\infty d\lambda\ \lambda^{k-1}e^{-\lambda}E\left(p; \alpha_r:\ q; \rho_s:\ \frac{z}{\lambda}\right) = E(p + 1; \alpha_r:\ q; \rho_s:\ z)$$

where $\alpha_{p+1} \equiv k$. Combining these two results with equation (52) gives for the integral $\mathscr{E}_s$

$$\mathscr{E}_s = \frac{\left(\frac{\sigma}{b}\right)^7 \zeta}{2\pi^{1/2}\Gamma(s+3/2)}\left\{5E\left[\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \ s+\frac{3}{2}: 3: \left(\frac{b}{\zeta\sigma}\right)^2\right] + 2E\left[\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \ s+\frac{3}{2}: 4: \left(\frac{b}{\zeta\sigma}\right)^2\right]\right.$$

$$\left. - 6E\left[\frac{9}{2}, \frac{5}{2}, \frac{3}{2}, \ s+\frac{3}{2}: 3: \left(\frac{b}{\zeta\sigma}\right)^2\right] + 2E\left[\frac{11}{2}, \frac{7}{2}, \frac{3}{2}, \ s+\frac{3}{2}: 4: \left(\frac{b}{\zeta\sigma}\right)^2\right]\right\} \qquad \left(\frac{b}{\sigma}\right) \geq 1 \qquad (53)$$

where the E functions have been reduced to their lowest order. This expression can now be used in equation (45) to give

$$\left\langle H_R^{(2)}\right\rangle = \frac{1}{4\Gamma(s+1)}\frac{\mu_1^2\mu_2^2}{\sigma^6 kT}\frac{T}{T_R}\left(\frac{\sigma}{b}\right)^7 \zeta\left\{5E\left[\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \ s+\frac{3}{2}: 3: \left(\frac{b}{\zeta\sigma}\right)^2\right] + 2E\left[\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \ s+\frac{3}{2}: 4: \left(\frac{b}{\zeta\sigma}\right)^2\right]\right.$$

$$\left. - 6E\left[\frac{9}{2}, \frac{5}{2}, \frac{3}{2}, \ s+\frac{3}{2}: 3: \left(\frac{b}{\zeta\sigma}\right)^2\right] + 2E\left[\frac{11}{2}, \frac{7}{2}, \frac{3}{2}, \ s+\frac{3}{2}: 4: \left(\frac{b}{\zeta\sigma}\right)^2\right]\right\} \qquad \left(\frac{b}{\sigma}\right) \geq 1 \qquad (54)$$

For impact parameters less than σ, $\mathscr{E}_s$ and, therefore, the result corresponding to equation (54) must be obtained by numerical integration. The typical behavior of $\left\langle H_R^{(2)}\right\rangle$ is illustrated in figure 6. It should be noted that, although $\left\langle H_R^{(2)}\right\rangle$ is continuous, it is sharply peaked at $b/\sigma = 1$.

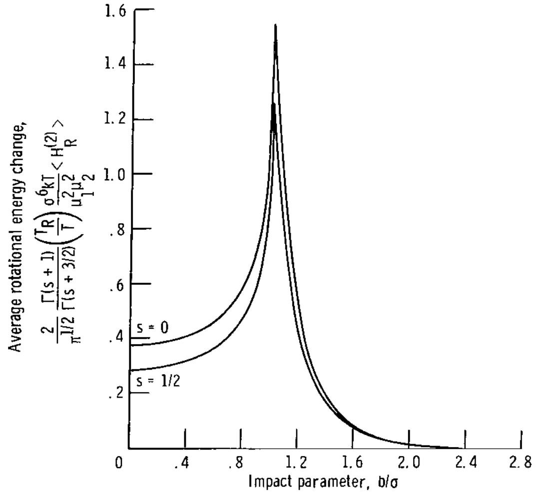

Figure 6. - Average change in dimensionless rotational energy as function of impact parameter. Mass distribution parameter, $\zeta^2 = 0.1$.

Evaluation of the Second Order Term $\left\langle (H_R^{(1)})^2 \right\rangle$

The evaluations of $\left\langle (H_R^{(1)})^2 \right\rangle$ closely parallels the discussion of the previous section and, therefore, some of the details will be omitted. The integrand of $H_R^{(1)}$ can be expressed in an appropriate form by combining the equations (A20), (A22), (19), and (20) to give

$$\Omega^1(t')H_R^0(t) = -\sum_{k=1}^{2} \frac{p_k^0(t)}{I_k} \frac{\partial V(t')}{\partial q_k^0(t')} \tag{55}$$

This may now be used to express $(H_R^{(1)})^2$ in the form

$$\begin{aligned} (H_R^{(1)})^2 &= \int\!\!\int_{-\infty}^{\infty} dt' \, dt'' \left[\Omega^1(t'')H_R^0(t)\right]\left[\Omega^1(t')H_R^0(t)\right] \\ &= \sum_{k,\,j=1}^{2} \int\!\!\int_{-\infty}^{\infty} dt' \, dt'' \, \frac{p_k^0}{I_k} \frac{p_k^0}{I_j} \frac{\partial V(t'')}{\partial q_j^0(t'')} \frac{\partial V(t')}{\partial q_k^0(t')} \end{aligned} \tag{56}$$

Upon evaluating the partial derivatives of the dipole-dipole interaction potential (9) and averaging the integrand of $(H_R^{(1)})^2$ over the orientations $q_1^0(0)$ and $q_2^0(0)$ we obtain the function

$$\begin{aligned} \bar{\mathcal{H}}(\omega^{(\pm)}, E, b, t', t'') &= (2\pi)^{-2} \int_{-\pi}^{\pi} dq_1^0(0) \int_{-\pi}^{\pi} dq_2^0(0) \left[\Omega^1(t'')H_R^0(t)\right]\left[\Omega^1(t')H_R^0(t)\right] \\ &= \left(\frac{\mu_1^2 \mu_2^2}{8}\right) \frac{\left\{\omega^{(-)2} \cos\left[\omega^{(-)}(t'' - t')\right] + 9\omega^{(+)2} \cos\left[\omega^{(+)}(t'' - t') - 2Q_2^0(t'') + 2Q_2^0(t')\right]\right\}}{\left[Q_1^0(t'')Q_1^0(t')\right]^3} \end{aligned} \tag{57}$$

This function $\overline{\mathscr{H}}$, although similar to the function $\mathscr{H}$ defined in (31), is not identical to $\mathscr{H}$. The next step in the calculation is to average $\overline{\mathscr{H}}$ over the rotational energy distribution and we then obtain

$$\frac{1}{\pi k T_R} \int_{-\infty}^{\infty}\!\! d\lambda^{(+)} \int d\lambda^{(-)} \overline{\mathscr{H}} \exp\left[- \frac{\left(\lambda^{(+)^2} + \lambda^{(-)^2} \right)}{kT_R} \right] = \frac{\mu_1^2 \mu_2^2 I^{(+)} kT_R}{8 I_1 I_2} \left(1 + \partial/\partial\epsilon\right)$$

$$\times \left\{ 1 + 9 \cos 2\left[Q_2(t') - Q_2(t'') \right] \right\} \frac{\exp\left[- \dfrac{\epsilon^2 (t'' - t')^2 I^{(+)} kT_R}{2 I_1 I_2} \right]}{\left[Q_1^0(t'') Q_1^0(t') \right]^3} \qquad (58)$$

The right side of this expression is identical to the right side of equation (37) apart from a factor $2kT_R$. If we now combine equation (58) with the results of the previous section we obtain the expression

$$\left\langle \left(H_R^{(1)}\right)^2 \right\rangle = 2kT_R \left\langle H_R^{(2)} \right\rangle = \frac{\pi^{1/2} \Gamma(s+3/2)}{\Gamma(s+1)} \frac{\mu_1^2 \mu_2^2}{\sigma^6} \int_0^{\infty} d\kappa \frac{\rho(\kappa) \kappa^2 \zeta}{\left(1 + \kappa^2 \zeta^2\right)^{s+3/2}} \qquad (59)$$

The Calculation of Z_{ROT} and Z'_{ROT}

Equation (1) can be used as a basis for the calculation of τ_R. The derivative dE_R/dt represents the change in rotational energy per collision averaged over the number of collisions per unit time. This is equivalent to the average change in rotational energy per collision, $\langle \Delta E_R \rangle_{Av}$ divided by τ_c, the mean time between collisions. Thus, at $t = 0$ equation (1) becomes

$$\frac{\langle \Delta E_R \rangle_{Av}}{\tau_c} = \left.\frac{dE_R}{dt}\right|_{t=0} = \frac{E_R(T) - E_R(t = 0)}{\tau_R} \qquad (60)$$

Assuming the molecules to be rotationally unexcited at $t = 0$ and solving for $\tau_c \tau_R^{-1}$ we find

$$Z_{ROT}^{-1} = \tau_c \tau_R^{-1} = \frac{1}{E_R(T)} \langle \Delta E_R \rangle_{Av} \qquad (61)$$

The calculation of $\langle \Delta E_R \rangle_{Av}$ includes only the contribution of trajectories with impact parameters out to some maximum impact parameter $\bar{b}$. All of the impact parameter dependence is contained in the integral $\mathcal{E}_s$, defined in equation (51). Because $\mathcal{E}_s$ goes to zero so rapidly, the integration can actually be extended to infinity with little error. We, therefore, define a function Θ_{sn} by

$$\frac{\Theta_{sn}(\zeta^2)}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} = \frac{n+1}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} \int_0^\infty \mathcal{E}_s(b/\sigma, \zeta^2) \left(\frac{b}{\sigma}\right)^n d\left(\frac{b}{\sigma}\right) \qquad (62)$$

where n can either take the value 0 or 1. The value $n = 0$ corresponds to a two-dimensional calculation while $n = 1$ corresponds to the "three-dimensional" case. In terms of Θ_{sn}, we can now write the expression for the change in rotational energy averaged over orientations, translational and rotational distribution functions, and impact parameters in the form

$$\langle \Delta E_R \rangle_{Av} = \frac{n+1}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} \int_0^\infty \langle \Delta E_R \rangle \left(\frac{b}{\sigma}\right)^n d\left(\frac{b}{\sigma}\right) \cong \frac{n+1}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} \int_0^\infty \langle H_R^{(2)} \rangle \left(\frac{b}{\sigma}\right)^n d\left(\frac{b}{\sigma}\right)$$

$$= \frac{\pi^{1/2}\Gamma(s+3/2)}{2\Gamma(s+1)} \frac{\mu_1^2 \mu_2^2}{\sigma^6 kT} \frac{\left(\frac{T}{T_R}\right)}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} \Theta_{sn}(\zeta^2) \qquad (63)$$

TABLE II. - NUMERICAL VALUES FOR

FUNCTION Θ_{sn}

Mass distribution parameter, ζ^2	Average rotational energy change per collision		$\Theta_{(1/2)0}/\Theta_{11}$
	$\Theta_{(1/2)0}$	Θ_{11}	
0	0	0	1.4443
2.0×10^{-3}	2.9884×10^{-1}	2.0691×10^{-1}	1.4207
4.0×10^{-3}	3.8473	2.7081	1.4207
6.0×10^{-3}	4.3908	3.1215	1.4066
8.0×10^{-3}	4.7823	3.4228	1.3972
1.0×10^{-2}	5.0827	3.6554	1.3905
2.0×10^{-2}	5.9327	4.3126	1.3757
3.0×10^{-2}	6.3115	4.5954	1.3734
4.0×10^{-2}	6.4967	4.7225	1.3757
5.0×10^{-2}	6.5819	4.7698	1.3799
7.5×10^{-2}	6.5876	4.7268	1.3937
1.0×10^{-1}	6.4675	4.5916	1.4086
1.5×10^{-1}	6.1259	4.2626	1.4371
2.0×10^{-1}	5.7738	3.9464	1.4631
2.5×10^{-1}	5.4490	3.6659	1.4864

Table II gives the function Θ_{sn} in tabular form.

To assist in the discussion of the function Θ_{sn}, let us reexamine equation (45). The parameter ζ^2 that appears in this equation is proportional to the parameter used by Sather and Dahler (refs. 13 and 14) in their rough sphere calculations. It differs from their parameter $4I/m\sigma^2$ only by an additional factor of $(T/4T_R)$. Therefore, the integrand of equation (45) has a moment of inertia dependence quite similar to the rough sphere results. This is particularly true for the case $s = 1/2$. Because of this fact and because of the sharply peaked behavior of $\mathscr{E}_s$, it is desirable to define a comparison function Θ_{sn}^o, analogous to Θ_{sn}, but based on the use of a density function $\kappa^2\rho^o(\kappa) = \delta(\kappa - 1)\delta(1 - b/\sigma)$ where $\delta(\kappa)$ is the Dirac delta function. This gives

$$\Theta_{sn}^o = \frac{(n+1)\zeta}{(1+\zeta^2)^{s+3/2}}$$

The function Θ_{sn}^o can be thought of as corresponding to the rigid sphere result for the model used in this paper. For comparison purposes, figure 7 gives plots of both Θ_{sn} and Θ_{sn}^o. From figure 7, it can be seen that averaging over the density function $\rho(\kappa)$ has the effect of shifting the maximum from relatively large values of ζ^2 in the function

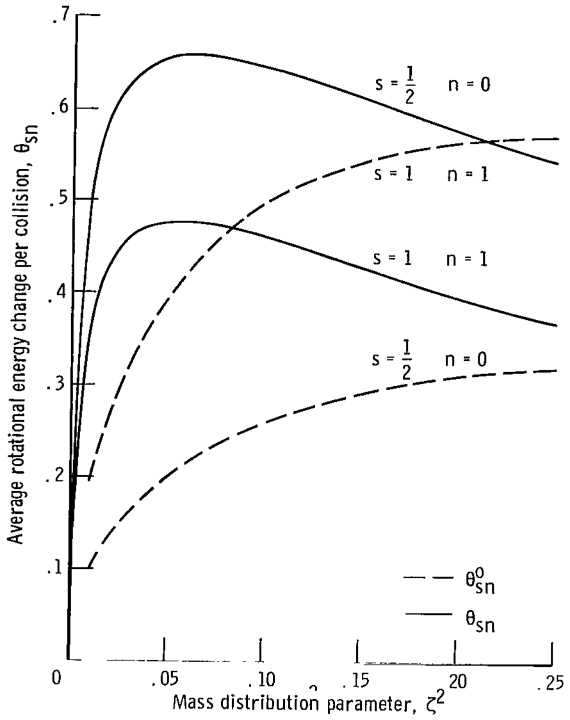

Figure 7. - A comparison of θ_{sn} and θ^0_{sn}.

Θ^0_{sn} to relatively small values of ζ^2 in the function Θ_{sn}. The net result is that Z_{ROT}, for this model, can be either an increasing or decreasing function of I depending upon whether ζ^2 lies to the left or to the right of the maximum.

We are now in a position to calculate Z_{ROT} from equation (61). The mean time between collisions, τ_c, is given by

$$\tau_c \begin{cases} = \dfrac{1}{2\nu\sigma^2}\sqrt{\dfrac{m}{2\pi kT}} & \text{(3-dimensions)} \\ \\ = \dfrac{1}{\nu\sigma}\sqrt{\dfrac{m}{2\pi kT}} & \text{(2-dimensions)} \end{cases} \tag{64}$$

where ν is the number density with dimensions appropriate to either two or there dimensions. Substituting this equation, together with equation (63) into equation (61) gives

$$Z_{ROT}^{-1} = \tau_c \tau_R^{-1} = \tau_c \frac{\left(\frac{dE_R}{dt}\right)_{t=0}}{E_R(T)} = \frac{\pi^{1/2}\Gamma(s+3/2)}{2\Gamma(s+1)} \left[\frac{\mu_1^2 \mu_2^2}{\sigma^6 kTE_R(T)}\right] \frac{\left(\frac{T}{T_R}\right)}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} \Theta_{sn}(\zeta^2) \qquad (65)$$

In the usual case the two colliding molecules are identical and, therefore, $\mu_1 = \mu_2 = \mu$ and $\sigma_1 = \sigma_2 = \sigma$. Also, we can write $E_R = \gamma kT/2$ where γ is the number of rotational degrees of freedom and is either 2 or 3. Thus, equation (65) can be written as

$$Z_{ROT}^{-1} = \frac{1}{\gamma} \pi^{1/2} \frac{\Gamma(s+3/2)}{\Gamma(s+1)} \left(\frac{\mu^2}{\sigma^3 kT}\right)^2 \frac{\left(\frac{T}{T_R}\right)}{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}} \Theta_{sn}(\zeta^2) \qquad (66)$$

The adjustable parameter $\bar{b}$ can be eliminated by considering a ratio of collision numbers. If, in addition, we consider the near equilibrium situation, we may set $T/T_R = 1$ to obtain

$$\frac{Z_{ROT}(1, T)}{Z_{ROT}(2, T_o)} = \frac{\gamma_1}{\gamma_2} \left(\frac{\mu_2}{\mu_1}\right)^4 \left(\frac{\sigma_1}{\sigma_2}\right)^{5-n} \left(\frac{T}{T_o}\right)^2 \frac{\Theta_{sn}(\xi_2^2)}{\Theta_{sn}(\xi_1^2)} \qquad (67)$$

where the notation $Z_{ROT}(1, T)$ represents the collision number of species 1 at a temperature T.

The equation (2) will serve as a basis for calculating Z'_{ROT}. The classical equivalent of the Wang Chang, Uhlenbeck, and DeBoer expression (ref. 24) for the volume viscosity κ can be written in our notation as

$$\kappa^{-1} = \frac{2\pi}{kT} \left(\frac{kT}{2\pi m}\right)^{1/2} \left(\frac{C_v}{C_{int}}\right)^2 \int_0^\infty db\, b \left\langle \left(\frac{\Delta E_R}{kT}\right)^2 \right\rangle \qquad (68)$$

Combining this equation with equation (2), the three-dimensional expression for τ_c (65), and using $\gamma k/2$ for C_{int} gives

$$(Z'_{ROT})^{-1} = \frac{(n+1)}{2\gamma} \int_0^\infty d\left(\frac{b}{\sigma}\right)\left(\frac{b}{\sigma}\right)^n \left\langle \left(\frac{\Delta E_R}{kT_R}\right)^2 \right\rangle \tag{69}$$

$n = 1, \; s = 1, \; T/T_R = 1$

Strictly speaking, the parameters n and s were unnecessarily introduced into this equation since the Wang Chang, Uhlenbeck, and DeBoer formula for κ requires both of these parameters to be unity. However, if we relax this restriction and permit the combination $n = 0$, $s = 1/2$ we will have a greater parallelism between the calculation of Z'_{ROT} and Z_{ROT}. The collision number Z'_{ROT} can then be given an analogous interpretation. That is, since $\left\langle(\Delta E_R)^2\right\rangle$ was estimated for a two-dimensional system, $n = 1$, $s = 1$, corresponds to a quasi three-dimensional calculation while $n = 0$, $s = 1/2$ represents a two-dimensional calculation.

We can now substitute for $\left\langle(\Delta E_R/kT_R)^2\right\rangle$ in equation (69) by using its perturbation approximation given in equation (59). If we then combine this result with the definition of the function Θ_{sn} given in equation (62) we find

$$(Z'_{ROT})^{-1} = \frac{1}{2\gamma} \frac{\pi^{1/2}\Gamma(s+3/2)}{\Gamma(s+1)} \frac{\mu_1^2\mu_2^2}{\sigma^6(kT)^2} \Theta_{sn}(\zeta^2) \tag{70}$$

Setting $\mu_1 = \mu_2$ and comparing this with the expression for Z_{ROT} given in equation (66) shows that within the level of approximation employed in the calculation we obtain the surprising result

$$Z_{ROT} = \frac{\left(\frac{\bar{b}}{\sigma}\right)^{n+1}}{2} Z'_{ROT} \tag{71}$$

Thus, both definitions give identical predictions about the dependence of the rotational collision number on the temperature, the dipole moment, and the moment of inertia.

COMPARISON WITH EXPERIMENT

It would be unrealistic to expect equations (66) or (70) to agree quantitatively with experiment in view of the approximate nature of the calculation. The best that one can hope for is a relative comparison based on equation (67), which holds equally well for

Z'_{ROT} and Z_{ROT} because of equation (71). Hence, attention will be confined to a comparison of equation (67) with experimental data.

The molecular diameter and the moment of inertia must be evaluated before the theoretical results (eq. (67)) can be compared with experimental data. The moment of inertia will be taken to be the arithmetic mean of a molecule's principle moments of inertia. O'Neal and Brokaw (ref. 33) suggest that σ be set equal to the viscosity collision diameter σ_η and calculated by the relation

$$\sigma^2 = \sigma_\eta^2 \equiv \frac{5}{16} \frac{\sqrt{\pi M k T}}{\pi \eta(T)} \tag{72}$$

In expression (72), $\eta(T)$ is the viscosity at a temperature T. O'Neal and Brokaw used σ_η only in the calculation of τ_c; I shall use the identification (72) for σ wherever it appears in the formulae. This use of σ_η for σ might be viewed as an attempt to account for the fact that the spherically symmetric short range repulsion, although rising abruptly, does not rise vertically as in a rigid sphere.

By using equation (72) and considering first the quasi-three-dimensional result ($s = 1$, $n = 1$), equation (67) takes the form

$$\frac{Z_{ROT}(1, T)}{Z_{ROT}(2, T_o)} = \frac{\gamma_1}{\gamma_2} \left(\frac{\mu_1}{\mu_2}\right)^4 \left(\frac{M_1}{M_2}\right) \left(\frac{T}{T_o}\right)^3 \left[\frac{\eta_2(T_o)}{\eta_1(T)}\right]^2 \frac{\Theta_{11}(2, T_o)}{\Theta_{11}(1, T)} \tag{73}$$

The variable ζ^2, required for the evaluation of Θ_{11}, is to be calculated as

$$\zeta^2 = \frac{16\pi}{5} \frac{\left(\frac{I}{M}\right) \eta(T)}{\sqrt{\pi M k T}} \tag{74}$$

Some qualitative comments can now be made concerning the behavior of equation (73). According to this equation, an increase in dipole moment decreases the collision number. Furthermore, since all the moment of inertia dependence is contained in ζ^2 and since the values of ζ^2 (as calculated from eq. (74)) lie to the left of the maximum in Θ_{11}, an increase in I causes a decrease in Z_{ROT}. Both of these results are in accord with experimental observations. Finally, Z_{ROT} increases with temperature when calculated by equation (73), however, because of the compensation due to viscosity, the increase is at a considerably lower rate than indicated by the explicit T^3 dependence. Based on some typical calculations, the increase is very nearly linear at the lower temperatures but becomes somewhat steeper as the temperature is increased. At present, there is sufficient uncertainty about the temperature behavior of Z_{ROT} so that one cannot conclude that equation (73) either agrees or disagrees with experiment.

A comparison between equation (73) and experimental results is made in tables III and IV. To evaluate equation (73), it was necessary to use the data of table I and, in addition, viscosity data. The viscosity data cited by Baker and Brokaw (refs. 1 and 2) were used in the evaluation of equation (73) for all molecules except SO_2, H_2S, HF, DF, and the fluoromethanes. For SO_2 and H_2S the viscosity was obtained by fairing a curve through the data contained in the references cited by Svehla (ref. 34). The HF viscosity was calculated by using the extrapolation formula of Posey (ref. 35). The viscosity cross section of DF was taken to be equal to HF. The viscosity data for the fluoromethanes was taken from Svehla's tabulation (ref. 34).

The theoretical temperature dependence of the rotational collision number for SO_2 and NH_3 are compared with experimental values in table III. Only these molecules could

TABLE III. - COMPARISON OF THEORETICAL AND EXPERIMENTAL TEMPERATURE DEPENDENCE OF Z_{ROT}

Temperature, K	$Z(T)/Z(T_0)$		
	Theoretical		Experimental
	Two-dimensional	Three-dimensional	
	SO_2		
300	1.00	1.00	[a]1.00
500	1.42	1.61	1.1 to 2.1
700	2.00	2.42	1.9 to 3.9
900	2.73	3.42	3.7 to 9.4
	NH_3		
311.2	1.00	1.00	[b]1.00
333.2	1.02	1.05	1.02
353.2	1.05	1.09	1.03
373.2	1.07	1.13	1.12
393.2	1.09	1.17	1.20
413.2	1.12	1.21	1.25
433.2	1.14	1.25	1.29
453.2	1.16	1.29	1.38
473.2	1.18	1.33	1.59

[a] Ref. 4.
[b] Ref. 5.

TABLE IV. - COMPARISON OF THEORETICAL AND EXPERIMENTAL Z_{ROT} FOR A GIVEN TEMPERATURE

	Temperature, K	Theoretical		Experimental
		Two-dimensional	Three-dimensional	
Z_{DCl}/Z_{HCl}	300.1	[b]0.54	[c]0.76	[a]0.43
	328.5	↓	.77	.50
	375.8	↓	↓	.56
	423.1	↓	↓	.60
	471.4	↓	↓	.62
Z_{D_2O}/Z_{H_2O}	381.2	[b]0.63	[c]0.75	[d]0.52
	426.1	↓	.76	----
	478.0	↓	.75	----
	525.6	↓	.76	----
Z_{ND_3}/Z_{NH_3}	300.0	[b]0.64	[c]0.78	[a]0.69
	329.1	↓	.79	.70
	374.6	↓	↓	.72
	424.2	↓	↓	.72
	424.2	↓	↓	.74
	474.5	↓	↓	.77
$Z_{^{15}NH_3}/Z_{NH_3}$	300.0	[b]1.05	[c]1.02	[a]1.05
	424.2	1.05	1.01	1.04
Z_{DF}/Z_{HF}	373.8	[b]0.58	[c]0.78	[e]0.44
	422.3	.58	.79	.41
$Z(H_2S, 298.3^\circ K)/$ $Z(H_2O, 381.2^\circ K)$	-----	[c]14.8		[f]11.6
$Z(H_2S, 298.3^\circ K)/$ $Z(HCl, 300.1^\circ K)$	-----	[c]2.9		[g]5.0
$Z(CH_2F_2, 300^\circ K)/$ $Z(CHF_3, 300^\circ K)$	-----	[c].56		[h].77
$Z(CH_2F_2, 300^\circ K)/$ $Z(CH_3F, 300^\circ K)$	-----	[c]1.08		[h].43

[a] Ref. 2.

[b] Modified Sather and Dahler (refs. 2, 13, and 14);
$Z_{ROT}^{-1} \propto (4I/M\sigma_\eta^2)/(1 + 4I/M\sigma_\eta^2)^2$.

[c] Eq. (60).

[d] Ref. 1.

[e] Ref. 3.

[f] Refs. 1 and 6.

[g] Refs. 2 and 6.

[h] Ref. 10.

be compared with theoretical results because the experimental data for the other molecules indicate that Z_{ROT} decreases with temperature. To put table III in a somewhat better perspective, it should be pointed out that the collision numbers obtained from the ammonia data of Baker and Brokaw (ref. 2) have a temperature dependence that is opposite to those of Srivastava and Das Gupta (ref. 5). Thus, it is somewhat surprising that the experimental and theoretical values agree as well as they do. In the light of the present uncertainties concerning the experimental data, this agreement must be viewed as largely fortuitous.

A comparison of isotope and dipole moment effects, as calculated from equation (73), is given in table IV. In addition, the results from the modified Sather and Dahler formula (ref. 33) are also given. Here, the agreement is not as good as was the case for table IV, in fact, some of the calculated numbers differ from the experimental results almost by a factor of two. In general, it can be said that equation (73) qualitatively mirrors the isotope and dipole moment effects, however, quantitative agreement between theory and experiment is lacking.

In addition to choosing values of σ and I, it is necessary to decide what values the indices s and n should take. The quasi-three-dimensional case corresponds to the choice $s = 1$ and $n = 1$ while the two-dimensional case corresponds to the choice $s = 1/2$ and $n = 0$. Up to now, we have only considered the "three-dimensional case." The relation of the two choices can be easily established from equation (67).

$$\frac{\left[\frac{Z_{ROT}(1, T)}{Z_{ROT}(2, T_o)}\right]_{2\text{-dim}}}{\left[\frac{Z_{ROT}(1, T)}{Z_{ROT}(2, T_o)}\right]_{3\text{-dim}}} = \frac{\sigma_1}{\sigma_2}\left[\frac{\Theta_{1/2\ 0}^{(2)}}{\Theta_{11}^{(2)}}\right]\left[\frac{\Theta_{11}^{(1)}}{\Theta_{1/2\ 0}^{(1)}}\right] \tag{75}$$

The parameter ζ^2 is generally less than 5×10^{-2} and, thus from table II, it follows that the Θ_{sn} in equation (75) produce differences of the order of 1 percent. The ratio of viscosity cross sections, on the other hand, can produce differences of the order of 10 percent or more. Since the viscosity cross sections of the isotopic pairs are generally taken to be equal at a given temperature, we can conclude that both the two- and "three-" dimensional cases will predict essentially the same moment of inertia dependence. However, because of the rather strong temperature dependence of the viscosity cross section, there will be a substantial difference in the predicted temperature dependence. In general, the two dimensional case displays a considerably slower increase of Z_{ROT} with temperature. This can be seen from the data in table III. It does appear that the "three" dimensional case agrees with the experimental results somewhat better than does the two-dimensional case.

CONCLUDING REMARKS

The calculations that were described in the previous sections show that the two definitions of a relaxation time are equivalent for our model, at least through third order in perturbation. Furthermore, a comparison with experimental values given in the literature seems to indicate that the calculated rotational collision number is in moderate agreement with experimental results.

The reason for the lack of better agreement between the theoretically and experimentally deduced effects of temperature, dipole moment, and moments of inertia on Z_{ROT} is problematical. In part, it may be due to the fact that the theoretical calculation was essentially two dimensional and not three dimensional as required by reality. In recent Monte Carlo calculations both Bunker and Blais (ref. 36) and Karplus and Raff (ref. 37) detected considerable differences between two- and three-dimensional results. A portion of the disagreement might possibly be a result of the data used in evaluating equation (73). For example, a 2 percent error in the viscosity ratio results in a 4 percent error in the ratio of Z_{ROT}. A similar error in the dipole moment ratio produces an 8 percent error in the Z_{ROT} ratio. Such errors are undoubtedly contributing factors. For example, the viscosity cross sections of isotopic pairs were generally taken to be equal. Only in the case of the pair H_2O and D_2O was any correction made. A third reason for the discrepancies is the apparent sensitivity of Z_{ROT} to relatively small experimental errors in thermal conductivity. Finally, some of the difficulties might possibly be a result of some deficiency in the theory used for extracting Z_{ROT} from thermal conductivity measurements. At present, it is impossible to assess the relative importance of each of these factors.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 18, 1969,
129-01-06-01-22.

APPENDIX A

CLASSICAL PERTURBATION THEORY

Garrido (refs. 21 and 22) has presented a formulation of classical mechanics in the interaction picture. Formally, the development is very similar to the corresponding treatment of the Dirac or interaction picture of quantum mechanics. For any classical system with the Hamiltonian

$$H = H_0 + V \tag{A1}$$

the solution to Hamilton's equations can be written in the form

$$\left.\begin{aligned} q &= q(p_0, q_0, t - t_0) \\ p &= 0(p_0, q_0, t - t_0) \end{aligned}\right\} \tag{A2}$$

where q_0 and p_0 are the values of the coordinates and momenta at the initial time t_0. The solution of Hamilton's equations for the unperturbed systems, characterized by the Hamiltonian H_0, can be written in a similar form

$$\left.\begin{aligned} q &= q^o(p_0, q_0, t - t_0) \\ p &= p^o(p_0, q_0, t - t_0) \end{aligned}\right\} \tag{A3}$$

Thus, it is assumed that the initial values of the coordinates and momenta for both the perturbed and the unperturbed system are identical.

The time evolution of any dynamical variable

$$F = F(q, p, t)$$

can easily be obtained for either the perturbed or the unperturbed system by substitutions of the appropriate solutions (A2) or (A3). For the perturbed system,

$$F(t) = F\left[q(p_0, q_0, t - t_0), p(p_0, q_0, t - t_0), t\right] \equiv U(t, t_0)F(q_0, p_0, t_0) \tag{A4}$$

and, similarly, for the unperturbed system,

$$F^o(t) = F\left[q^o(p_0, q_0, t - t_0), p^o(p_0, q_0, t - t_0), t\right] = U^o(t, t_0)F(q_0, p_0, t_0) \tag{A5}$$

The evolution operators U and U^0 defined in equations (A4) and (A5) have the usual properties

$$\left.\begin{aligned} U(t, t'')U(t'', t') &= U(t,t') \\ U(t, t) &= 1 \\ U^{-1}(t, t') &= U(t', t) \end{aligned}\right\} \tag{A6}$$

From a consideration of infinitesimal time translations, one obtains the differential equations satisfied by the time evolution operator

$$\frac{dU(t, t_0)}{dt} = \Omega(t)U(t, t_0) = U(t,t_0)\Omega(t_0) \tag{A7}$$

where the operator $\Omega(t)$ is defined by

$$\Omega(t) = \frac{\partial}{\partial t} - [H,] = \frac{\partial}{\partial t} + \frac{\partial H}{\partial p}\frac{\partial}{\partial q} - \frac{\partial H}{\partial q}\frac{\partial}{\partial p} \tag{A8}$$

The second equality in equation (A7) follows from the fact that for any operator $O(t)$

$$O(t) = U(t, t_0)O(t_0)U(t_0, t) \tag{A9}$$

Analogous equations can be written for the unperturbed system. The solution of equation (A7) can be easily obtained from the integral form of this equation.

$$U(t, t_0) = 1 + \int_{t_0}^{t} dt'\Omega(t')U(t', t_0) = 1 + \int_{t_0}^{t} dt'\ U(t', t_0)\Omega(t_0) \tag{A10}$$

Using the first equality in equation (A10), we get as the iterative solution

$$U(t, t_0) = P \exp\left[\int_{t_0}^{t} dt'\ \Omega(t')\right] \tag{A11}$$

where P is the Dyson time ordering operator. Using the second equality in equation tion (A10), we get the alternate result

$$U(t,\ t_0) = \exp\left[(t - t_0)\Omega(t_0)\right]$$

Therefore, the operator $U(t,\ t_0)$ is nothing more than a Taylor expansion about t_0.

To apply these results to perturbation, it is only necessary to observe that equations (A4) and (A5) can be combined to give

$$F(t) = U(t,\ t_0)F(q_0,\ p_0,\ t_0) = U(t,\ t_0)U^o(t_0,\ t)U^o(t,\ t_0)F(q_0,\ p_0,\ t_0)$$

or

$$F(t) = S(t)F^o(t) \tag{A12}$$

where the operator $S(t)$ is defined as

$$S(t) \equiv U(t,\ t_0)U^o(t_0,\ t) \tag{A13}$$

From the differential equations for U and U^o (eq. (A7)), one readily obtains the differential equation satisfied by S

$$\frac{dS}{dt} = S(t)\Omega^1(t) \tag{A14}$$

where the operator $\Omega^1(t)$ is a Poisson bracket

$$\Omega(t) - \Omega^o(t) = \Omega^1(t) = -\left[V,\ \right] = \frac{\partial V}{\partial p^o(t)}\frac{\partial}{\partial q^o(t)} - \frac{\partial V}{\partial q^o(t)}\frac{\partial}{\partial p^o(t)} \tag{A15}$$

and V is evaluated along the unperturbed trajectories. The iterative solution of the integral equation obtained from equation (A14) can be written as

$$S(t) = \mathscr{P}\exp\left[\int_{t_0}^{t} dt'\ \Omega^1(t')\right] = 1 + \int_{t_0}^{t} dt'\ \Omega^1(t')$$

$$+ \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\ \Omega^1(t'')\Omega^1(t') + \ldots \tag{A16}$$

The time ordering operator $\mathscr{P}$ in equation (A16) orders time-dependent operators in sense opposite to that of the Dyson time ordering operator P.

$$\mathscr{P}\Omega^1(t')\Omega^1(t'') \begin{cases} = \Omega^1(t')\Omega^1(t'') & t' < t'' \\ = \Omega^1(t'')\Omega^1(t') & t'' < t' \end{cases} \tag{A17}$$

The relation between F(t) and $F^o(t)$ given by equation (A12) can now be rewritten by using the iterative expansion of the operator S(t) given by equation (A16).

$$F(t) = \sum_{n=0}^{\infty} F^{(n)}(t) = F^{(0)}(t) + F^{(1)}(t) + F^{(2)}(t) + \ldots \tag{A18}$$

where the first three terms are given explicitly by

$$\left.\begin{aligned} F^{(0)}(t) &= F^o(t) \\ F^{(1)}(t) &= \int_{t_0}^{t} dt'\ \Omega^1(t')F^o(t) \\ F^{(2)}(t) &= \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\ \Omega^1(t'')\Omega^1(t')F^o(t) \end{aligned}\right\} \tag{A19}$$

To evaluate the integrals given in equation (A19) one must be able to determine the effect of $\Omega^1(t')$ on the function $F^o(t)$. This is possible when one knows the solution to the unperturbed problem in the form of equation (A3). Using equations (A5), (A15), and the chain rule for differentiation, we obtain

$$\Omega^1(t')F^o(t) = \frac{\partial V}{\partial p^o(t)}\left[\frac{\partial F^o(t)}{\partial q^o(t)}\frac{\partial q^o(t)}{\partial q^o(t')} + \frac{\partial F^o(t)}{\partial p^o(t)}\frac{\partial p^o(t)}{\partial q^o(t')}\right]$$

$$- \frac{\partial V}{\partial q^o(t')}\left[\frac{\partial F^o(t)}{\partial q^o(t)}\frac{\partial q^o(t)}{\partial p^o(t')} + \frac{\partial F^o(t)}{\partial p^o(t)}\frac{\partial p^o(t)}{\partial p^o(t')}\right]$$

or, upon rearranging,

$$\Omega^{1}(t')F^{o}(t) = \frac{\partial F^{o}(t)}{\partial q^{o}(t)}\,\Omega^{1}(t')q^{o}(t) + \frac{\partial F^{o}(t)}{\partial p^{o}(t)}\,\Omega^{1}(t')p^{o}(t)$$

Explicitly indicating that more than one set of coordinates and momenta may enter the problem, we have for the special case where F depends upon momenta alone, the result

$$\Omega^{1}(t')F^{o}(t) = \sum_{k} \frac{\partial F^{o}(t)}{\partial p_{k}^{o}(t)}\,\Omega^{1}(t')p_{k}^{o}(t) \tag{A20}$$

The second order term is somewhat more complicated

$$\Omega^{1}(t'')\Omega^{1}(t')F^{o}(t) = \sum \frac{\partial F^{o}(t)}{\partial p_{k}^{o}(t)}\,\Omega^{1}(t'')\Omega^{1}(t')p_{k}^{o}(t) + \sum_{k,l} \frac{\partial^{2} F^{o}(t)}{\partial p_{l}^{o}(t)\,\partial p_{k}^{o}(t)}\,\Omega^{1}(t'')p_{l}^{o}(t)\Omega^{1}(t')p_{k}^{o}(t) \tag{A21}$$

When the perturbation only depends on coordinates, we can write

$$\Omega^{1}(t')p_{k}^{o}(t) = -\sum \frac{\partial V(t')}{\partial q_{l}^{o}(t')}\,\frac{\partial p_{k}^{o}(t)}{\partial p_{l}^{o}(t')} \tag{A22}$$

and the second order term

$$\Omega^{1}(t'')\Omega^{1}(t')p_{k}^{o}(t) = \sum \frac{\partial V(t'')}{\partial q_{j}^{o}(t'')}\,\frac{\partial}{\partial p_{j}^{o}(t'')}\left[\sum \frac{\partial V(t')}{\partial q_{l}^{o}(t')}\,\frac{\partial p_{k}^{o}(t)}{\partial p_{l}^{o}(t')}\right]$$

$$= \sum_{j,l,i} \frac{\partial V(t'')}{\partial q_{j}^{o}(t'')}\,\frac{\partial^{2} V(t')}{\partial q_{i}^{o}(t')\partial q_{l}^{o}(t')}\,\frac{\partial q_{i}^{o}(t')}{\partial p_{j}^{o}(t'')}\,\frac{\partial p_{k}^{o}(t)}{\partial p_{l}^{o}(t')} + \sum_{j,l} \frac{\partial V(t'')}{\partial q_{j}^{o}(t'')}\,\frac{\partial V(t')}{\partial q_{l}^{o}(t')}\,\frac{\partial^{2} p_{k}^{o}(t)}{\partial p_{j}^{o}(t'')\partial p_{l}^{o}(t')} \tag{A23}$$

APPENDIX B

EVALUATION OF A(ϵ) AND B(ϵ)

The function $A(\epsilon)$, defined in equation (34), contains an integral of the convolution or Faltung type

$$\mathscr{I} = \iint_{-\infty}^{\infty} dt_1\, dt_2\, f(t_1) g(t_2) r(t_1 - t_2) \tag{B1}$$

where $r(t)$ is the Gaussian function

$$r(t) = \exp\left(\frac{-\epsilon^2 t^2}{\tau_1^2}\right) \tag{B2}$$

The function $B(\epsilon)$, defined in equation (35), will also contain a linear combination of integrals of the type in equation (B1) if the trigonometric function in its integrand is expanded. The convolution theorem (ref. 38) can be used to rewrite equation (B1) in terms of the Fourier transforms of the functions in its integrand

$$\mathscr{I} = (2\pi)^{1/2} \int_{-\infty}^{\infty} d\kappa F^*(\kappa) G(\kappa) R(\kappa) \tag{B3}$$

where the asterisk is used to denote complex conjugation and where the Fourier transforms are defined as

$$G(\kappa) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} dt\; g(t) e^{i\kappa t} \tag{B4}$$

For the case at hand, the functions $f(t)$, $g(t)$, and $r(t)$ possess a definite symmetry being either even or odd functions of t. Furthermore, $f(t)$ and $g(t)$ will always have the same symmetry. For an even function the Fourier transform is identical to the Fourier cosine transform while for odd functions it differs from the Fourier sine transform by a factor of $i = (-1)^{1/2}$. The sine and cosine transforms are defined by the expression

$$G_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty dt\, g(t) \left\{\begin{matrix}\sin \kappa t\\ \cos \kappa t\end{matrix}\right\} \tag{B5}$$

Thus, for example, the Fourier transform of the Gaussian (B2) is

$$R(\kappa) = R_c(\kappa) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty dt\, e^{-(\epsilon t/\tau_1)^2} \cos \kappa t = 2^{1/2} \left(\frac{\tau_1}{2\epsilon}\right) e^{-(\kappa\tau_1/2\epsilon)^2} \tag{B6}$$

Combining this result with equation (B3) and using the symmetry properties of the sine and cosine transforms gives

$$\mathcal{J} = 4\pi^{1/2} \left(\frac{\tau_1}{2\epsilon}\right) \int_0^\infty d\kappa\, F_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa) G_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa) e^{-(\kappa\tau_1/2\epsilon)^2} \tag{B7}$$

In the evaluation of $A(\epsilon)$ and $B(\epsilon)$ it is still necessary to integrate integrals of the type (eq. (B7)) over $x = E/kT$. This can be accomplished without knowing the functional form of the transforms F and G. This is possible because the functions f and g depend only on the combination (t/τ) where τ contains all the x dependence (eq. (37)). This means that with an appropriate change of integration variable equation (B5) takes the form

$$G_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa) = \tau \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty dz\, g(z) \left\{\begin{matrix}\sin \kappa\tau z\\ \cos \kappa\tau z\end{matrix}\right\} = \tau G_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa\tau) \tag{B8}$$

Using this equation, together with an analogous expression for the transform F, and making the change of variable $\kappa\tau \rightarrow \kappa$ gives

$$\mathcal{J}(x) = 4\pi^{1/2} \left(\frac{\tau_1}{2\epsilon}\right)\tau \int_0^\infty d\kappa\, F_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa) G_{\left\{\begin{matrix}s\\c\end{matrix}\right\}}(\kappa) e^{-\kappa\tau_1/2\epsilon\tau)^2}$$

Now, averaging $\mathcal{J}(x)$ over the energy will give

$$\frac{1}{\Gamma(s+1)}\int_0^\infty dx\, x^s e^{-x}\mathcal{J}(x) = 4\pi^{1/2}\,\frac{\Gamma(s+1/2)}{\Gamma(s+1)}\,\tau_2^2\int_0 d\kappa\, F_{\left\{ s \atop c \right\}}(\kappa)\, G_{\left\{ s \atop c \right\}}(\kappa)\,\frac{\left(\dfrac{\tau_1}{2\epsilon\tau_2}\right)}{\left[1+\left(\dfrac{\kappa\tau_1}{2\epsilon\tau_2}\right)^2\right]^{s+1/2}} \tag{B9}$$

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