

Theory of Microwave Nonresonant Absorption and Relaxation in Gases

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A quantum derivation is given of nonresonant absorption and dielectric and magnetic relaxation in gases with molecules which have diagonal electric or magnetic dipole matrix elements. General expressions for the shape and width of pressure-broadened nonresonant lines are obtained by solving a master equation for the polarization. Relaxation by bimolecular collisions which change the magnetic (orientational) and total-angular-momentum quantum numbers of the dipoles is treated in the impact approximation. The case of weak collisions which change these quantum numbers by one or two units is solved in detail; intermediate and strong collisions which cause much larger quantum changes are considered qualitatively. Formulas are derived for computing collision cross sections from known intermolecular interactions for weak collisions. On comparing experimental results for symmetric-top gases with the theory, it is concluded that strong collisions are responsible for the relaxation process.

I. INTRODUCTION AND SUMMARY

CLASSICALLY speaking, symmetric-top¹ and certain diatomic² molecules have a component of the permanent dipole moment in the direction of the total angular momentum. This dipole component, which is stationary (nonrotating) in space except for reorientations by molecular collisions, gives rise to a nonresonant or Debye-type spectra in gases at low pressure, where collisions are bimolecular. In quantum mechanics, reorientations are equivalent to transitions among the various spatially degenerate quantum states. Since such transitions are produced by anisotropic intermolecular interactions between a pair of colliding molecules, the study of nonresonant absorption in gases is capable of yielding valuable information on such interactions, provided the relation between the relaxation time and the pertinent molecular parameters is known.

Nonresonant spectra have been analyzed within the framework of the Debye equation, obtained from the Van Vleck-Weisskopf equation specialized for zero frequency.^{1,2} In these equations the linewidth or relaxation frequency appears as a parameter to be determined by experiment. Since it is clear that the linewidth in general must be a function of rotational state, it has been assumed that the nonresonant shape may be represented as a sum of Debye equations, each of which depends on the rotational state. It is the object of this work to derive expressions for nonresonant line shape and relaxation rate.

The most complete study of the impact theory of spectral line shape for isolated lines has been given by Anderson³ and extended by Tsao and Curnutte.⁴ This theory which has had some success in accounting for the width of resonant lines⁵ has failed in its application to

nonresonant lines.⁶ However, Ben-Reuven⁷ has recently emphasized that the Anderson theory should not apply to nonresonant lines which should be regarded as composed of many overlapping lines at zero frequency. The first consistent treatments of overlapping lines in the theory of pressure broadening were made by Baranger,⁸ and by Kolb and Griem.⁹ Their results were later re-derived as a particular case of a more general theory by Fano.¹⁰ Using the theories of Baranger, Kolb and Griem, and Fano, Ben-Reuven⁷ has treated pressure broadening in both the resonant and nonresonant microwave spectra of gases.

In this paper, we start with a master equation governing the distribution of dipoles among the rotational states and derive an expression for the frequency-dependent polarization associated with the diagonal dipole matrix elements. This type of treatment is based upon a method frequently adopted in the theory of dielectric and magnetic relaxation.^{11,12} It differs from the method of Ben-Reuven⁷ and gives additional insight into the nature of the relaxation process.

After a physical picture of the polarization process is presented in Sec. II, a rate equation for the polarization is developed in Sec. III. General expressions for the shape and width of nonresonant lines in gases are derived in Sec. IV. The relaxation rate expressed in terms of cross sections is treated in the impact approximation in Sec. V. Formulas for the cross section for a variety of intermolecular potentials are obtained in Sec. VI by a perturbation expansion. The resulting selection rules allow changes in the magnetic and total-angular-momentum quantum numbers of only one or two units.

(McGraw-Hill Book Company, Inc., New York, 1955), pp. 355-369.

⁶ G. Birnbaum (to be published).

⁷ A. Ben-Reuven, *Phys. Rev.* **145**, 7 (1966).

⁸ M. Baranger, *Phys. Rev.* **111**, 481 (1958); **111**, 494 (1958); **112**, 855 (1958).

⁹ A. C. Kolb and H. Griem, *Phys. Rev.* **111**, 514 (1958).

¹⁰ U. Fano, *Phys. Rev.* **131**, 259 (1963).

¹¹ C. J. Gorter and R. de L. Kronig, *Physica* **3**, 1009 (1936); R. de L. Kronig, *Physica* **5**, 65 (1938).

¹² J. H. Van Vleck and V. F. Weisskopf, *Rev. Mod. Phys.* **17**, 227 (1945).

¹ G. Birnbaum, *J. Chem. Phys.* **27**, 360 (1957).

² A. A. Maryott and S. J. Kryder, *J. Chem. Phys.* **31**, 617 (1959) for NO, and A. A. Maryott and G. Birnbaum, *ibid.* **32**, 686 (1960) for O₂.

³ P. W. Anderson, *Phys. Rev.* **76**, 647 (1949).

⁴ C. J. Tsao and B. Curnutte, *J. Quant. Spectry. Radiative Transfer* **2**, 41 (1962).

⁵ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*

Collisions associated with such transitions are called weak, and the corresponding relaxation rate for dipole-dipole interaction is found to be much smaller than the experimental values (Sec. VII). The case of strong collisions which cause large changes in the rotational state of the dipoles, and the role of weak and strong collisions in resonant and nonresonant absorption are discussed in Sec. VIII.

To check the theory as well as to discuss certain of its aspects, the spin-lattice relaxation rate in certain types of paramagnetic crystals is obtained in Appendix A. Certain sums of matrix elements which are needed in the development of the theory are evaluated in Appendices B and C.

II. THE STATIONARY COMPONENT OF THE DIPOLE MOMENT

Consider a symmetric top molecule whose rotational state is specified by the quantum numbers, J , K , and M . In units of \hbar , $[J(J+1)]^{1/2}$ is the total angular momentum, K is the component of angular momentum along the symmetry axis, and M is the projection of the total angular momentum J_z along a given axis. The vector relation of these angular momenta is illustrated in Fig. 1. In the absence of electric or magnetic fields, the states $M = J \cdots -J$ are degenerate. The permanent dipole moment \mathbf{u} lies along the symmetry axis \mathbf{K} and, classically speaking, has a component $\mathbf{u}K/[J(J+1)]^{1/2}$ collinear with \mathbf{J} . As a consequence, symmetric top molecules may be expected to interact with electric fields in a manner analogous to the behavior of magnetic spins in magnetic fields.

Consider an isolated molecule in state J and in a definite eigenstate M in the direction of a linearly polarized electric field, $F = F_0 e^{i\omega t}$. The stationary or diagonal component of the dipole moment in the direction of the applied field is given by¹³

$$\mu_{JKM} = \mu \langle J, K, M | \cos\theta | J, K, M \rangle = \mu KM / J(J+1), \quad (1)$$

where μ is the permanent dipole moment. If, as is assumed here, the angular frequency ω is not resonant with any pair of rotational levels, the applied field cannot induce rotational transitions. In addition, it is clear

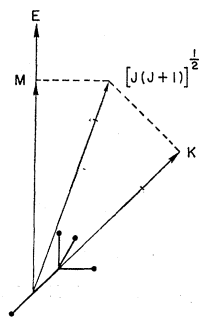


FIG. 1. Vector diagram of the angular momenta for a symmetric top molecule. The molecule represented is, for example, CH_3Cl .

that the applied field cannot exert a torque and, therefore, reorient the molecule. However, these transitions, e.g., $M \rightarrow M'$, $J \rightarrow J'$ and $M, J \rightarrow M', J'$, can occur because of molecular collisions.¹⁴ In terms of (1), these transitions signify, respectively, a reorientation of the stationary component of the dipole moment, a change in its magnitude, and both. Detailed balancing in the presence of the applied field preferentially weights those transitions which increase the dipole moment in the direction of the field, and consequently, the gas becomes polarized.

We should note that the interaction between the dipole and perturber depends on space quantization with respect to the line joining the two molecules. This line moves in space as the perturber passes by, turning through an angle $\leq 180^\circ$ during a complete passage. If the interaction is adiabatic, i.e., if the collisions are slow and the splitting of the degeneracy by the intermolecular force is large, the dipole remains in the same M state with respect to the collision axis and effects a complete reorientation about the space fixed axis.¹⁵ Such collisions are not considered in evaluating the cross sections. The sudden approximation is used where one regards the intermolecular perturbation as the cause of transitions to other eigenstates of the unperturbed Hamiltonian.

III. THE RATE EQUATION FOR THE POLARIZATION

The Debye formula for the reorientational relaxation of magnetic dipoles in paramagnetic solids has been derived quantum mechanically by Kronig¹¹ for weak collisions and by Van Vleck and Weisskopf¹² for collisions of arbitrary strength. Their derivations are based on solving appropriate rate equations governing the polarization in the magnetic substates belonging to a given spin state. Extending their method, we obtain in this section equations for nonresonant absorption in gases for collisions of arbitrary strength, which change both the magnetic and total-angular-momentum quantum numbers.

Wang Chang and Uhlenbeck¹⁶ (WC-U) have presented a semiclassical treatment of transport theory in dilute gases where the translational motion is considered classically and internal motions quantum mechanically. They use a distribution function $f_i(v_i, t)$ for each quantum state i which refers to the entire set of quantum numbers necessary to specify the internal state of the molecule. Here we let the polar molecule be designated by $i = 1$, and the perturbing molecule by $i = 2$. The posi-

¹⁴ The transition $K \rightarrow K'$ is strictly forbidden for all interactions considered here; for simplicity, this quantum number will often be suppressed.

¹⁵ H. Margenau and M. Lewis, *Rev. Mod. Phys.* **31**, 569 (1959).

¹⁶ C. S. Wang Chang and G. E. Uhlenbeck, in *Molecular Theory of Gases and Liquids*, edited by J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird (John Wiley & Sons, Inc., New York, 1954), pp. 501-506.

¹³ R. de L. Kronig, *Proc. Nat. Acad. Sci.* **12**, 608 (1926).

tion coordinates in the distribution function are suppressed since only uniform gases are considered. This function is defined in such a way that $f_i(v_i)dv_i$ represents the density of molecules in state i in the velocity element dv_i at a time t . Each distribution function satisfies its own Boltzmann equation which for negligible external forces may be written as

$$\frac{df_1}{dt} = \sum_{1'22'} \left[\int \int f_{1'}(v_{1'}) f_{2'}(v_{2'}) v_{1'2'} \sigma_{12,1'2'}(v_{1'2'}) dv_{1'} dv_{2'} - \int \int f_1(v_1) f_2(v_2) v_{12} \sigma_{1'2',12}(v_{12}) dv_1 dv_2 \right], \quad (2)$$

where v_{12} represents the initial relative velocity of molecules 1 and 2 before a collision in which the final relative velocity is $v_{1'2'}$. The cross section $\sigma_{1'2',12}(v_{12})$ refers to a collision in which the molecules initially in states 1 and 2 end up in states 1' and 2'.

The Boltzmann equation derived by WC-U has been discussed by Taxman¹⁷ and Snider,¹⁸ the latter emphasizing that this equation applies when the internal states are nondegenerate and the corresponding density matrix is diagonal. With spatial degeneracy, the initial state of a molecule may be any linear combination of degenerate states belonging to the same energy. Snider¹⁸ has derived a Boltzmann-type equation for this case which includes nondiagonal terms in the distribution function. However, Tolhoek and de Groot¹⁹ have shown that when the Hamiltonian of a system is invariant for rotations, the density matrix of the ensemble remains diagonal in the degenerate quantum numbers. In the system under study, the unperturbed Hamiltonian is spherically symmetric, and the effect of collisions is also spherically symmetric, i.e., there is no preferential direction for the velocity of the perturbers. Consequently, Eq. (2) which has only populations and neglects off-diagonal terms is sufficiently general for our purpose.

Since the distribution function $f_1(v_1)$ can be represented as a product of the function f_1 , the density of molecules in state 1, and $F(v_1)$, the normalized velocity distribution function, Eq. (2) may be written in the form

$$df_1/dt = \sum_{1'} (f_{1'} A_{11'} - f_1 A_{11'}). \quad (3)$$

$A_{11'}$ is the probability per unit time that molecule 1 will make a transition from state 1 to 1' accompanied by an unspecified transition of the perturber. This transition rate is given by

$$A_{11'} = \sum_{22'} f_2 \int \int g(v) v dv \sigma_{1'2',12}, \quad (4)$$

where $g(v)$ is the distribution function for the initial relative velocity. Note that the ensemble of perturbers represents the heat bath.

¹⁷ N. Taxman, Phys. Rev. **110**, 1235 (1958).

¹⁸ R. F. Snider, J. Chem. Phys. **32**, 1051 (1960).

¹⁹ H. A. Tolhoek and S. R. de Groot, Physica **15**, 833 (1949).

Equation (3) describes the system with an applied electric or magnetic field, $F = F_0 e^{i\omega t}$, provided f and A are functions of this field. Then detailed balancing is preserved when¹²

$$A_{11'} \exp[-(E_1 - \mu_1 F)/kT] = A_{11'} \exp[-(E_{1'} - \mu_{1'} F)/kT], \quad (5)$$

where E_1 is the internal energy, μ_1 is the diagonal dipole matrix element in the direction of the field, and F is the instantaneous value of the field at collision. To the first power in the field, a Taylor expansion gives

$$A_{11'} = A_{11'}^0 + (\partial A_{11'}/\partial F_0)_{F_0=0} F_0, \quad (6)$$

$$f_1 = f_1^0 + \sigma_1 F_0, \quad (7)$$

where the superscript zero denotes the absence of a field. The population f_1 and population per unit field σ_1 are functions of time; f_1^0 is time-independent. It is assumed that the perturber does not interact with the field, and consequently $f_2 \equiv f_2^0$. Then to terms linear in the applied field, Eq. (3) becomes

$$d\sigma_1/dt = \sum_{1'} [\sigma_{1'} A_{11'}^0 - \sigma_1 A_{11'}^0 + (e^{i\omega t}/kT)(f_1^0 \mu_1 A_{11'}^0 - f_{1'}^0 \mu_{1'} A_{11'}^0)]. \quad (8)$$

With the subscript 1 replaced by the quantum numbers J, M ,¹⁴ the polarization in state J is given by

$$P_J = F_0 \sum_M \mu_{JM} \sigma_{JM}. \quad (9)$$

Then multiplying Eq. (8) by $F_0 \mu_{JM}$ and summing over M , we have the rate equation for the polarization in the J th state,

$$dP_J/dt = F_0 \sum_{J'MM'} [\sigma_{J'M'} \mu_{JM} A_{JM,J'M'}^0 - \sigma_{JM} \mu_{JM} A_{J'M',JM}^0 + (e^{i\omega t}/kT)(f_{JM}^0 \mu_{JM}^2 A_{JM,J'M'}^0 - f_{J'M'}^0 \mu_{J'M'}^2 A_{J'M',JM}^0)]. \quad (10)$$

IV. THE COMPLEX DIELECTRIC CONSTANT AND RELAXATION RATE

In the absence of the field, the Hamiltonian of the system is spherically symmetric and the transition probability cannot depend on how the axis of quantization is selected. As a consequence, several authors^{3,8,12} have obtained a relation of the form

$$\sum_M \mu_{JM} A_{JM,J'M'}^0 = \mu_{J'M'} R_{JJ'}, \quad (11)$$

where the reduced matrix $R_{JJ'}$ is independent of magnetic quantum numbers. With Eqs. (9) and (11), Eq. (10) becomes

$$dP_J/dt = \sum_{J'} (P_{J'} R_{JJ'} - P_J \sum_{M'} A_{J'M',JM}^0 + (F/kT) \sum_M f_{JM}^0 \mu_{JM}^2 \sum_{M'} A_{J'M',JM}^0 - (F/kT) \sum_{M'} \mu_{J'M'}^2 f_{J'M'}^0 R_{JJ'}), \quad (12)$$

where the sum $\sum_{M'} A_{J'M',JM}^0$ is independent of magnetic quantum numbers.^{19,20} Multiplying Eq. (11) by

²⁰ See Appendix II and note from Eq. (38) that $A_{J'M',JM}^0 \propto \langle |T_{J'M',JM}|^2 \rangle_0$.

$\mu_{J'M'}$ and summing over M' , we obtain for $R_{JJ'}$

$$R_{JJ'} = \frac{\sum_{MM'} \mu_{JM} \mu_{J'M'} A_{JM, J'M'}^0}{\sum_{M'} \mu_{J'M'}^2}. \quad (13)$$

The the last two terms in Eq. (12) may be put in the form

$$\left(\sum_M f_{JM}^0 \mu_{JM}^2 \right) \left(\frac{\sum_{M''M'} \mu_{JM''} \mu_{J'M'} A_{J'M', JM''}^0}{\sum_{M''} \mu_{JM''}^2} \right) \quad (14)$$

by noting that f_{JM}^0 is independent of M , i.e., $f_{JM}^0 = f_{J'}^0/(2J+1)$, and by using the relation

$$f_{J'M'}^0 A_{JM, J'M'}^0 = f_{JM}^0 A_{J'M', JM}^0.$$

With some rearrangement, (14) may be written as

$$\Delta\omega_J \sum_M f_{JM}^0 \mu_{JM}^2,$$

where

$$\Delta\omega_J = \sum_{J'M'} A_{J'M', JM}^0 (1 - \mu_{J'M'}/\mu_{JM}). \quad (15)$$

In view of Eqs. (14) and (15), Eq. (12) becomes

$$\frac{dP_J}{dt} = \sum_{J'} \left[P_J \left(\frac{P_{J'}}{P_J} R_{JJ'} - \sum_{M'} A_{J'M', JM}^0 \right) + \frac{F}{kT} \Delta\omega_J \sum_M f_{JM}^0 \mu_{JM}^2 \right]. \quad (16)$$

Using the relation $dP_J/dt = i\omega P_J$, we obtain from Eq. (16),

$$P_J = \frac{F}{kT} \sum_M f_{JM}^0 \mu_{JM}^2 \frac{\Delta\omega_J}{i\omega + \Delta\omega_J}, \quad (17)$$

where $\Delta\omega_J'$ is given by

$$\Delta\omega_J' = \sum_{J'} ((P_{J'}/P_J) R_{JJ'} - \sum_{M'} A_{J'M', JM}^0). \quad (18)$$

An expression for $\Delta\omega_J'$ approximately in the form of Eq. (15), namely,

$$\Delta\omega_J' = \sum_{J'M'} A_{J'M', JM}^0 \left(1 - \frac{g_{J'}(\omega) \mu_{J'M'}}{g_J(\omega) \mu_{JM}} \right), \quad (19)$$

where

$$g_J(\omega) = \Delta\omega_J / (i\omega + \Delta\omega_J), \quad (20)$$

may be obtained by using Eqs. (13) and (14). Since the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ is related to the polarization by

$$\epsilon - 1 = (4\pi/F) \sum_J P_J, \quad (21)$$

we have from Eq. (17) that

$$\epsilon - 1 = \frac{4\pi}{kT} \sum_{JM} f_{JM}^0 \mu_{JM}^2 \frac{\Delta\omega_J}{\Delta\omega_J' + i\omega}. \quad (22)$$

When $\omega=0$, $\Delta\omega_J' = \Delta\omega_J$ and Eq. (22) gives

$$\epsilon'(0) - 1 = (4\pi/kT) \sum_{JM} f_{JM}^0 \mu_{JM}^2, \quad (23)$$

i.e., the usual expression for the static dielectric constant.¹⁸

Despite its simple appearance, Eq. (22) is extremely complicated since $\Delta\omega_J'$ is a function of the shape factors $g_J(\omega)$ and $g_{J'}(\omega)$. However, this equation may be simplified in several cases. If the probability for J transitions is negligible compared with that for M transitions, the solution of Eq. (16) is the Debye equation, namely,

$$\epsilon_J - 1 = \frac{4\pi \sum_M f_{JM}^0 \mu_{JM}^2}{kT} \frac{\Delta\omega_J}{\Delta\omega_J + i\omega}, \quad (24)$$

where $\Delta\omega_J$ is given by

$$\Delta\omega_J = \sum_{M'} A_{JM', JM}^0 (1 - \mu_{JM'}/\mu_{JM}). \quad (25)$$

Relaxation in paramagnetic crystals is an example of this case and is treated in Appendix A to illustrate the application of Eq. (25).

Consider next collisions so strong that all final orientations of the dipole are equally likely. In this case the transition rate will be independent of magnetic quantum numbers and the second and fourth terms on the right side of Eq. (10) will be equal to zero since $\sum_M \mu_{JM} = 0$. The vanishing of these terms means that the probability of a given dipole returning to its initial state in a single collision is negligible. The complex dielectric constant is now represented by a sum of Debye equations.

Numerous experiments have shown that the dielectric relaxation spectrum in gases has very nearly the simple Debye shape.^{1,2} It is therefore reasonable to make the approximation $g_{J'}(\omega)/g_J(\omega) \simeq 1$, in which case the complex dielectric is represented by a sum of Debye equations,

$$\epsilon - 1 = \frac{4\pi}{kT} \sum_{JM} f_{JM}^0 \mu_{JM}^2 \frac{\Delta\omega_J}{\Delta\omega_J + i\omega}, \quad (26)$$

where $\Delta\omega_J$ is given by Eq. (15). For the purpose of calculation, it is convenient to introduce the quantity $L_{J'J}$ defined by

$$\sum_{M'} \mu_{J'M'} A_{J'M', JM}^0 = \mu_{JM} L_{J'J} \sum_{M'} A_{J'M', JM}^0. \quad (27)$$

Then Eq. (15) assumes the form

$$\Delta\omega_J = \sum_{J'} (\sum_{M'} A_{J'M', JM}^0) (1 - L_{J'J}). \quad (28)$$

An expression for $L_{J'J}$ is derived in Appendix C. The assumption of strong collisions means that $L_{J'J}$ is negligible, whereas for weak collisions, $L_{J'J}$ is nearly equal to one and greatly reduces the contribution of such collisions to the relaxation frequency. Thus the contribution to the polarization arising from transitions in which dipoles leave a given state can be largely canceled by the polarization arising from reverse transitions.

Since dielectric-loss measurements have shown that the frequency distribution has nearly the Debye shape,^{1,2}

it is reasonable to expand Eq. (26) in a power series. A first approximation produces a Debye term plus a small correction term.⁷ The relaxation frequency in the Debye term is the intensity weighted average,

$$\langle \Delta\omega \rangle = \frac{\sum_{JM} f_{JM}^0 \mu_{JM}^2 \sum_{J'M'} A_{J'M',JM}^0 (1 - \mu_{J'M'}/\mu_{JM})}{\sum_{JM} f_{JM}^0 \mu_{JM}^2} \quad (29)$$

The numerator of this equation may be rearranged as

$$\sum_{J'M',JM} f_{JM}^0 A_{J'M',JM}^0 \frac{1}{2} (\mu_{JM} - \mu_{J'M'})^2.$$

Then using Eq. (4) for the transition rate and Eq. (29), we obtain

$$\langle \Delta\omega \rangle = \sum_{1'1} f_1^0 \sum_{2'2} f_2^0 \int_0^\infty v g(v) dv \sigma_{1'2',12} \times \frac{1}{2} (\mu_1 - \mu_{1'})^2 / \sum_1 f_1^0 \mu_1^2, \quad (30)$$

which is identical with Ben-Reuven's⁷ equation derived by a different method. (As before subscript 1 means JM , $1'$ means $J'M'$, and 2 and $2'$ refer to the initial and final states of the perturbing molecule.) Equation (30) clearly shows that only collisions which change the expectation value of the dipole in the direction of the applied field contribute to the relaxation frequency.

V. CROSS SECTION IN THE SUDDEN APPROXIMATION

General expressions for the transition probability and cross section in the sudden approximation are developed in this section. Only an outline of the derivation sufficient to define terms is presented since this derivation has been discussed by a number of authors.^{3,4,8,21}

The Hamiltonian for two molecules, whose translational motion is described by a classical trajectory, is given by

$$H(t) = H_1 + H_2 + H_c(t). \quad (31)$$

H_1 and H_2 are the unperturbed Hamiltonians of molecules 1 and 2, containing only their internal coordinates, and $H_c(t)$ is the intermolecular interaction. In the interaction picture, the Schrödinger equation of motion is formally solved by²²

$$\Psi(t) = U(t, t_0) \Psi(t_0). \quad (32)$$

The propagator $U(t, t_0)$ is defined by

$$U(t, t_0) = P \exp \left[-\frac{i}{\hbar} \int_{t_0}^t H_c'(t') dt' \right], \quad (33)$$

where

$$H_c'(t) = e^{(i/\hbar)(H_1+H_2)t} H_c(t) e^{(-i/\hbar)(H_1+H_2)t}. \quad (34)$$

²¹ R. B. Bernstein and K. H. Kramer, Theoretical Chemistry Institute, The University of Wisconsin, 1965 (unpublished).

²² E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1962), Chap. 17.

In Eq. (33) P is the time-ordering operator which makes operators act in the order prescribed by the time in their argument. If $H_c(t)$ commutes with $H_1 + H_2$, then Eq. (33) with the time-ordering operator removed solves the equation of motion. The requirement that $[H_1 + H_2, H_c(t)] = 0$ demands for all levels that $E_\beta - E_\alpha = 0$, where $E_\beta = E_{1'} + E_{2'}$ and $E_\alpha = E_1 + E_2$. However, it has been argued that for the particular levels considered, it is only necessary that²¹

$$|E_\beta - E_\alpha| \ll \hbar v / b_0, \quad (35)$$

where b_0 is the collision diameter and v is the relative velocity. Assuming that the inequality expressed by (35) holds, we have for the transition probability $1,2 \rightarrow 1',2'$,

$$|T_{1'2',12}|^2 = |\langle 1'2' | \exp[-(i/\hbar) \int_{t_0}^t H_c'(t') dt'] | 12 \rangle|^2. \quad (36)$$

The cross section for the transition $1,2 \rightarrow 1',2'$ is given by the integral

$$\sigma_{1'2',12} = \int_0^\infty |T_{1'2',12}(d\sigma)|^2 d\sigma, \quad (37)$$

where $d\sigma$ is an element of the cross section. The meaning of Eq. (37) is that the collisions are characterized according to the paths followed by the molecules; then corresponding to each element of cross section there is a definite transition probability. Since the integral $\int d\sigma$ implies an average over all direction angles of the colliding molecules relative to the polarization direction, Eq. (37) may be represented by

$$\sigma_{1'2',12} = \int_0^\infty 2\pi b db \langle |T_{1'2',12}(b)|^2 \rangle_\Omega, \quad (37a)$$

where b is the impact parameter or distance of closest approach, and $\langle \rangle_\Omega$ represents the average over all collision directions. However, since the collisions occur with equal probability in all directions (in the absence of the applied field), $\langle \rangle_\Omega$ is simply an average over the unit sphere. (See Appendix B.) This average is taken over the direction angles of molecule 1, since $|T_{1'2',12}|^2$ must be summed over all initial and final degenerate states of molecule 2, and such a double sum is independent of the orientation of molecule 2.

With Eq. (37a), the transition rate given by Eq. (4) becomes

$$A_{1'1}^0 = \sum_{2'2} f_2^0 \int_0^\infty g(v) v dv \int_0^\infty 2\pi b db \langle |T_{1'2',12}|^2 \rangle_\Omega. \quad (38)$$

The quantity $f_2^0 v 2\pi b db dt$ is the probability that a collision of type πb^2 occurs in the element of area $2\pi b db$ in a time dt . The interval dt is chosen large compared with the duration of collision, b/v , but small compared

with the interval between collisions so that it contains at most a single collision. For this reason, the limits of integration t and t_0 in Eq. (36) can be replaced by $\pm\infty$.

VI. CROSS SECTION FOR WEAK COLLISIONS

When collisions are weak, i.e., $\hbar^{-1}\int_0^\infty H_c(t)dt \ll 1$, Eq. (36) may be expanded in a power series. To terms of second order, the T matrix becomes

$$|T_{\beta\alpha}^{(1)}|^2 = |\langle\beta|\int_{-\infty}^\infty H_c(t)e^{i\omega(\beta\alpha)t}dt|\alpha\rangle|^2, \quad (39)$$

where β represents the final states $1'$, $2'$ and α the initial states 1 , 2 . $H_c(t)$ can be expressed as a sum of terms of the form⁴

$$C_{\lambda_1\lambda_2}{}^{k_1k_2}(t)Y_{\lambda_1}{}^{k_1}(1)Y_{\lambda_2}{}^{k_2}(2), \quad (40)$$

where the Y 's are the spherical harmonics of the rotational coordinates of the molecules. The time dependence of $H_c(t)$ due to the translational motion of the molecules is contained in $C(t)$ so that the time integration can be performed independently of the matrix elements. Hence, the general form of the matrix element for two symmetric top molecules is

$$\sum_{\substack{k_1k_2 \\ \lambda_1\lambda_2}} a(\lambda k j)\langle J_2'K_2'M_2', J'K'M' | Y_{\lambda}{}^k(1) \\ \times Y_{\lambda_2}{}^{k_2}(2) | J_2K_2M_2, JKM \rangle. \quad (41)$$

For simplicity, the subscript 1 indicating molecule 1 is omitted. The coefficients $a(\lambda k j)$ depend, besides, on the coefficients C in the expansion of H_c , also the results of the time integration. They therefore depend on the J 's as indicated by the single index j .

The matrix elements of the spherical harmonics can be evaluated in terms of the Clebsch-Gordan coefficients,

$$\langle J'K'M' | Y_{\lambda}{}^k(\theta, \phi) | JKM \rangle = \left[\frac{(2J+1)(2k+1)}{4\pi(2J'+1)} \right]^{1/2} \\ \times C(JkJ'; KOK)C(JkJ'; M\lambda M'). \quad (42)$$

The matrix element for the transition in the reverse direction is Eq. (42) with the primed and unprimed quantities interchanged. Using Eqs. (41) and (42), we obtain

$$|T_{\beta\alpha}^{(1)}|^2 = \sum_{\substack{k_1k_2 \\ \lambda_1\lambda_2}} |a(k\lambda j)|^2 \frac{(2J+1)(2k+1)}{4\pi(2J'+1)} C(JkJ'; M\lambda M')^2 \\ \times C(JkJ'; KOK)^2 \frac{(2J_2+1)(2k_2+1)}{4\pi(2J_2'+1)} \\ \times C(J_2k_2J_2'; K_2OK_2)^2 C(J_2k_2J_2'; M_2\lambda_2M_2')^2. \quad (43)$$

Summing Eq. (43) over magnetic quantum numbers and averaging over all directions of collisions, we find, using

Eq. (II.4), that

$$\sum_{M'M_2M_2'} \langle |T_{\beta\alpha}^{(1)}|^2 \rangle_{\Omega} = [(2J_2+1)/16\pi^2] \sum_{\substack{k_1k_2 \\ \lambda_1\lambda_2}} |a(k\lambda j)|^2 \\ \times C(JkJ', KOK)^2 C(J_2k_2J_2', K_2OK_2)^2. \quad (44)$$

Note that on substituting Eq. (44) in Eq. (38), the product $(2J_2+1)$ and $f_2^0 = f_{JM}^0$ gives f_J^0 .

It is convenient to define the quantity

$$S_{J_2', J_2, J_2J} = (2J_2+1)^{-1} \sum_{M'M_2M_2'} \langle |T_{\beta\alpha}^{(1)}|^2 \rangle_{\Omega}. \quad (45)$$

Summing Eq. (45) over all final values of J_2 , we have

$$S_{J', J_2J}(b) = \sum_{J_2'} S_{J_2', J_2, J_2J}(b) = \frac{B_n(J', J_2J)}{b^{2n-2}}. \quad (46)$$

The matrix elements are represented by B_n , and b^{-2n+2} is the result of the time integration of the translational motion of the molecules.⁴ The integer n depends on the intermolecular potential as shown in Table I.

On the basis of Eqs. (37a) and (46), the cross section associated with the transition $J \rightarrow J'$, summed over all magnetic substates and final rotational states of molecule 2, assumes the form

$$\sigma_{J', J_2J} = 2\pi \int_0^\infty b db \frac{B_n(J', J_2J)}{b^{2n-2}}. \quad (47)$$

Suppose that at the kinetic diameter b_k , $S(b_k) \ll 1$. Then if it is assumed that from $b=0$ to $b=b_k$, Eq. (46) has the value $S(b_k)$, Eq. (47) gives

$$\sigma_{J', J_2J} = \pi \frac{n-1}{n-2} \frac{B_n(J', J_2J)}{b_k^{2n-4}}. \quad (48)$$

In most cases, however, the interaction is so strong that $S(b)=1$ at intermolecular distance greater than the kinetic diameter. Since $S(b)$, essentially a transition probability, is obtained by a perturbation expansion, it should be restricted to values much less than one. Nevertheless, to evaluate Eq. (47) we make the same approximation as in the Anderson-Tsao and Cornutte theory of pressure broadening.^{3,4} Thus $S(b)$ is de-

TABLE I. Intermolecular potentials.

n	Potential	Order of spherical harmonic ^a	
		k_1	k_2
3	dipole-dipole	1	1
4	dipole-quadrupole	1	2
5	quadrupole-quadrupole	2	2
6	dipole-induced dipole	2	0

^a $Y_{\lambda_1}{}^{k_1}, Y_{\lambda_2}{}^{k_2}$.

terminated by Eq. (46) from $b = \infty$ to b_0 , where

$$S(b_0) = 1, \quad (49)$$

and is assumed to be one from $b = b_0$ to $b = 0$. Then Eq. (47) gives

$$\sigma_{J', J_2 J} = \pi((n-1)/(n-2)) [B_n(J', J_2 J)]^{1/(n-1)}. \quad (50)$$

Note that the integration produces $B_n^{1/(n-1)}$ rather than B_n , as in Eq. (48), and interchanging the order of summing over the quantum numbers and integrating over the impact diameter gives different results. Because the reaction of the internal motion on the translatory motion is neglected in the present approximation,²³ the averaging over paths and states should be independent and consequently the order of averaging may be interchanged.²⁴ The result showing that the order of averaging is significant arises apparently from the integration of a transition probability obtained by perturbation theory into the region of strong interaction.

VII. WEAK COLLISIONS. COMPARISON OF THEORY AND EXPERIMENT FOR DIPOLE-DIPOLE INTERACTION

To evaluate Eq. (47) for the cross section, it is necessary to consider specific intermolecular forces and to compute the collision integrals with respect to a given set of coordinates. The interaction may be evaluated in any convenient coordinate system, however, since the cross section is averaged over all collision directions.

Consider the quantity

$$|a(k\lambda j)|^2 = \left| \int_{-\infty}^{\infty} C_{\lambda\lambda_2}^{kk_2}(t) e^{i\omega(\beta\alpha)t} dt \right|^2, \quad (51)$$

where $C(t)$ depends on time through the intermolecular distance. We save the labor of evaluating Eq. (51) by noting that Tsao and Curmutte⁴ have calculated on the basis of a straight-line collision path a quantity $S_2(b)_{\text{outer}, i}$ related to our $\sum_{J' J_2'} S_{J_2' J', J_2 J}$. On comparing their Eq. (108) and our Eq. (46), we find that

$$\sum_{J' J_2'} S_{J_2' J', J_2 J}(b) = 2S_2(b)_{\text{outer}, i}. \quad (51a)$$

Then for dipole-dipole interaction in self-broadening, we obtain

$$S_{J_2' J', J_2 J}(b) = (16/9)(\mu^2/\hbar v b^2)^2 \times C(J_1 J'; K_0 K)^2 C(J_2 J_2'; K_2 O K_2)^2, \quad (52)$$

for the condition $\omega(\alpha\beta)b/v \ll 1$, where v is the mean relative velocity.

From Eqs. (28), (38), and (50), we obtain for the cross

section

$$\sigma_{J J_2} = \pi((n-1)/(n-2)) \times \sum_{J'} [B_n(J', J_2 J)]^{1/(n-1)} (1 - L_{J' J}), \quad (53)$$

where $L_{J' J}$ is given by Eq. (III.9). From the orthogonality of the Clebsch-Gordan coefficients, the sum over J_2' in Eq. (52) is unity; then Eq. (53) is evaluated as

$$\sigma_J = \frac{4}{3} \frac{\mu^2}{\hbar v} \left\{ \frac{1}{J(J+1)} \frac{K}{[J(J+1)]^{1/2}} + \frac{1}{(2J+1)^{1/2}} \left[\left(1 - \frac{K^2}{(J+1)^2}\right)^{1/2} - \left(1 - \frac{K^2}{J^2}\right)^{1/2} \right] \right\}. \quad (54)$$

The first term within the curly brackets arises from the $J, M \rightarrow J, M \pm 1$ transitions, and the second and third terms arise from the $J, M \rightarrow J+1, M \pm 1$ and $J, M \rightarrow J-1, M \pm 1$ transitions, respectively. To make comparison with experiment, the intensity-weighted average given by Eq. (30) should be used. However, it is sufficiently accurate for our purpose to take a Boltzmann average of the quantities in Eq. (54). Taking as values typical for a number of symmetric top molecules, $\mu = 10^{-18}$ esu, $v = 5 \times 10^4$ cm/sec, $\langle J^2 \rangle = 200$, $\langle K^2/J^2 \rangle = 0.2$ we find from Eq. (54) that the average diameter associated with the relaxation process is less than 1 Å, about an order of magnitude smaller than the experimental values shown in Table II.

VIII. STRONG COLLISIONS

To examine the effect of strong collisions, the transition probability given by Eq. (36) must be used. This transition probability has been evaluated by Bernstein

TABLE II. Nonresonant, rotational, and kinetic collision diameters of symmetric top molecules.

Gas	μ^a esu $\times 10^{-18}$	Nonres. diam ^b Å	Rotat. diam Å	Kinetic diam, Å	
				From critical vol or temp ^f	From vis- cosity
CH ₃ F	1.81	6.5	14.2 ^e	4.0	4.08
CH ₃ Cl	1.87	7.2	16.1 ^d	4.3	
CH ₃ Br	1.80	7.8		4.5	
CH ₃ I	1.65	8.5		4.7	
CH ₃ CN	3.96	12.4			
CHF ₃	1.65	5.3	16.2 ^e	4.2	
NH ₃	1.47	7.7	13.8 ^e		3.44
ND ₃	1.51	6.9			

^a A. A. Maryott and F. Buckley, Natl. Bur. Std. (U.S.) Cir. No. 537 (1953).

^b From Ref. 1 with the exception of NH₃ [B. Bleaney and J. H. N. Loubser, Proc. Phys. Soc. (London) 63, 483 (1950)] and ND₃ [G. Birnbaum and A. A. Maryott, Phys. Rev. 92, 270 (1953)].

^c The $J=0 \rightarrow 1$ transition of CH₃F and the $J=1 \rightarrow 2$ transition of CHF₃; O. R. Gillian, H. D. Edwards, and W. Gordy, Phys. Rev. 75, 1014 (1949).

^d The $J=0 \rightarrow 1$ transition; G. R. Bird, Phys. Rev. 95, 1686 (1954).

^e The $J=3, K=3$ inversion line; B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) 60, 540 (1948).

^f P. G. T. Fogg, P. H. Hanks, and J. D. Lambert, Proc. Roy. Soc. (London) A219, 497 (1955).

^g J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Liquids and Gases* (John Wiley & Sons, Inc., New York, 1954), Table 8.6-1.

²³ The net change in rotational energy is much smaller than the relative kinetic energy.

²⁴ J. Van Kranendonk, dissertation, University of Amsterdam, 1952, pp. 16-18 (unpublished).

and Kramer^{21,25} for collisions between a polar diatomic molecule and an atom. They found that with increasing strength of interaction, the selection rules obtained on the basis of a perturbation approximation, i.e., $\Delta M = \pm 1, \pm 2, \Delta J = \pm 1, \pm 2$, become progressively weakened, and more and more forbidden channels open up. In this process, as the impact parameter b is decreased from large values, successive transitions become important, reach a peak probability, then decrease in significance. It is found that at a value of b greater than the kinetic diameter, the individual transition probabilities become essentially randomized, with expectation values given by the reciprocal of the number of channels. Such transition probabilities are certainly independent of magnetic quantum numbers, and as shown in Sec. IV, $L_{J,J} = 0$. Then the line width $\Delta\omega_J$ is simply equal to the collision rate A_{J^0} for transitions out of the initial state, i.e., there is no negative term reducing the effect of A_{J^0} . It seems clear then that strong collisions must be mainly responsible for the observed nonresonant collision diameters shown in Table II.

It is interesting to compare the role of molecular impacts in the pressure broadening of rotational lines and nonresonant lines. In the former case, the collisions are considered strong when they cause the rotational transitions $\Delta J = \pm 1, \pm 2$, because such transitions represent a complete interruption of the radiation process. The collision diameters associated with such transitions are not only much larger than the kinetic diameter, but also, as shown in Table II, larger than the nonresonant values. We have seen that the contribution of such transitions to the relaxation frequency in nonresonant absorption is negligible, and that it is the stronger interactions at closer intermolecular distances which are needed to produce large reorientations and changes in the J states. In resonant absorption, on the other hand, once the radiating molecule has undergone a rotational transition, further transitions at closer distances can do no more than the original transition, i.e., completely interrupt the radiation process. In view of this, it is apparent that the study of nonresonant relaxation in gases provides a means of investigating the powerful intermolecular forces that exist between molecules in close encounters.

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APPENDIX A: RELAXATION IN PARAMAGNETIC CRYSTALS

It is instructive to obtain the spin-lattice relaxation rate in certain paramagnetic crystals by the method of this paper. Kronig¹¹ considered an ensemble of spins which have a stationary state with a $(2J+1)$ -fold de-

generacy, corresponding to $2J+1$ possible orientations when space quantized. This degeneracy is assumed to be completely removed by an external magnetic field; however, the splitting is assumed to be small compared with kT . The $2J+1$ sublevels of every spin have a value of the diagonal matrix element of the magnetic moment given by

$$\mu_{JM} = \mu_J M. \quad (\text{A.1})$$

The spins are coupled with the elastic vibrations of the crystal which cause quantum jumps of the spins between sublevels with values of M differing by one unit. The resulting transition rate is given by

$$A_{JM', JM^0} = BC(J1J; M\lambda M')^2, \quad (\text{A.2})$$

where B is a constant independent of the quantum numbers and λ has the values ± 1 . In the case of a gas, the transition rate is proportional to $|a(k, \lambda, j)|^2 \times C(JkJ'; M\lambda M')^2$, where $a(k, \lambda, j)$, which arises from the time integration of the molecular path, depends on λ [see Eq. (43)].

According to Eqs. (25) and (A.2),¹¹ the relaxation rate is given by

$$\Delta\omega = B \sum_{\lambda M'} C(J1J; M\lambda M')^2 (1 - \mu_{JM'} / \mu_{JM}). \quad (\text{A.3})$$

By the orthogonality of the Clebsch-Gordan coefficients, the sum of the first term in Eq. (A.3) is one, provided λ is allowed to have the value zero, although there is no diagonal matrix element. However, Eq. (A.3) shows that for the transition $M \rightarrow M$ there is no change in the dipole matrix element and the contribution of this transition to $\Delta\omega$ vanishes. In the case of a gas, because of the factor $a(k, \lambda, j)$, we cannot use the orthogonality relation in summing over λ and M' . Instead we sum over M' and average over directions of collision.

Using Eqs. (C.8) and (C.9), we find that

$$\begin{aligned} \sum_{\lambda M'} \mu_{JM'} C(J1J; M\lambda M')^2 \\ = \mu_{JM} [J(J+1) - 1] / J(J+1), \end{aligned} \quad (\text{A.4})$$

and consequently

$$\Delta\omega = B / [J(J+1)]. \quad (\text{A.5})$$

This is exactly Kronig's result since he uses $A_{M\pm 1, M^0} = B'(J \mp M)(J \pm M + 1)$ instead of Eq. (A.2), and consequently, $B = 2J(J+1)B'$. Note that $\Delta\omega$ rapidly decreases with increasing J .

APPENDIX B: EVALUATION OF

$$\sum_{M'} \langle |T_{J'M', JM}|^2 \rangle_{\Omega}$$

Consider the equation,

$$\Lambda = \sum_{M'} \langle |T_{J'M', JM}|^2 \rangle_{\Omega}, \quad (\text{B.1})$$

²⁵ K. H. Kramer and R. B. Bernstein, J. Chem. Phys. **40**, 200 (1964).

where the axis of quantization is the direction of the applied field, and the average is over the unit sphere. In a rotated coordinate system, we have

$$|T_{J'M',JM}|^2 = \sum_{\mu\mu'\mu''\mu'''} T_{J'\mu',J\mu} T_{J'\mu'',J\mu'''}^* \times D_{\mu M}^J D_{\mu' M'}^{J*} D_{\mu'' M'}^{J*} D_{\mu'' M'}^{J*}, \quad (\text{B.2})$$

where $D_{\mu M}^J$ is the rotation matrix, and μ designates the spatial quantization in the rotated coordinate system. The sum over M' gives

$$\sum_{M'} |T_{J'M',JM}|^2 = \sum_{\mu\mu'\mu''\mu'''} T_{J'\mu',J\mu} \times T_{J'\mu'',J\mu'''}^* D_{\mu M}^J D_{\mu' M'}^{J*} \delta_{\mu\mu'} \delta_{\mu''\mu'''}. \quad (\text{B.3})$$

The average of Eq. (B.3) over the unit sphere gives²⁶

$$\begin{aligned} \Lambda &= (2J+1)^{-1} \sum_{\mu\mu'\mu''\mu'''} T_{J'\mu',J\mu} T_{J'\mu'',J\mu'''}^* \delta_{\mu\mu'} \delta_{\mu''\mu'''} \\ &= (2J+1)^{-1} \sum_{\mu\mu'} |T_{J'\mu',J\mu}|^2, \end{aligned} \quad (\text{B.4})$$

i.e., Λ is independent of magnetic quantum numbers. Consequently, the T matrix may be evaluated in any convenient coordinate system. It is evident from the preceding development that

$$\sum_M \langle |T_{J'M',JM}|^2 \rangle_\Omega = (2J'+1)^{-1} \sum_{\mu\mu'} |T_{J'\mu',J\mu}|^2. \quad (\text{B.5})$$

APPENDIX C: EVALUATION OF

$$\sum_{M'} \mu_{J'M'} \langle |T_{J'M',JM}|^2 \rangle_\Omega$$

We wish to evaluate the sum in Eq. (27) and obtain an expression for $L_{J'J}$. From Eqs. (38) and (43), we see that the dependence of $A_{J'M',JM}^0$ on the projection quantum numbers M and M' is entirely contained in the Clebsch-Gordan coefficient $C(JkJ'; M\lambda M')$. In essence, then, we must evaluate

$$\gamma = \sum_{M'} M' \langle C(JkJ'; M\lambda M')^2 \rangle_\Omega, \quad (\text{C.1})$$

where $\mu_{J'M'} = M' \mu_{J'}$.

The symmetry relation of the Clebsch-Gordan co-

efficients gives²⁷

$$\begin{aligned} C(JkJ'; M\lambda M')^2 \\ = ((2J'+1)/(2J+1)) C(J'kJ; M', -\lambda, M)^2. \end{aligned} \quad (\text{C.2})$$

Then with the relation²⁸

$$\begin{aligned} M' C(J'kJ; M', -\lambda, M) &= \sum_{J''} \langle J''M'' | J_z' | JM \rangle \\ &\times C(J'kJ''; M', -\lambda, M), \end{aligned} \quad (\text{C.3})$$

Eq. (III.1) becomes

$$\begin{aligned} \gamma &= \frac{2J'+1}{2J+1} \frac{1}{8\pi^2} \int d\Omega \sum_{M'} C(J'kJ; M', -\lambda, M) \\ &\times \sum_{J''} \langle J''M'' | J_z' | JM \rangle C(J'kJ''; M', -\lambda, M). \end{aligned} \quad (\text{C.4})$$

Equation (C.4) vanishes in summing over M' and averaging over the unit sphere unless $J''=J$. Then since²⁸

$$\begin{aligned} J(J+1) \langle JM | J_z' | JM \rangle \\ = \frac{1}{2} M [J(J+1) + J'(J'+1) - k(k+1)], \end{aligned} \quad (\text{C.5})$$

Eq. (C.4) is evaluated as

$$\begin{aligned} \gamma &= M \left[\frac{1}{2} \frac{J(J+1) + J'(J'+1) - k(k+1)}{J(J+1)} \right] \\ &\times \sum_{M'} \langle C(JkJ', M\lambda M')^2 \rangle_\Omega. \end{aligned} \quad (\text{C.6})$$

In view of Eqs. (43) and (C.6), where the quantity within the square brackets is designated by $L_{J'J}$, we obtain the relation

$$\begin{aligned} \sum_{M'} \mu_{J'M'} \langle |T_{J'M',JM}|^2 \rangle_\Omega \\ = M \mu_{J'} L_{J'J} \sum_{M'} \langle |T_{J'M',JM}|^2 \rangle_\Omega. \end{aligned} \quad (\text{C.7})$$

Then using Eq. (1) and remembering that $K'=K$, we have

$$\begin{aligned} \sum_{M'} \mu_{J'M'} \langle |T_{J'M',JM}|^2 \rangle_\Omega \\ = \mu_{JM} L_{J'J} \sum_{M'} \langle |T_{J'M',JM}|^2 \rangle_\Omega, \end{aligned} \quad (\text{C.8})$$

where

$$L_{J'J} = \frac{1}{2} \frac{J(J+1) + J'(J'+1) - k(k+1)}{J'(J'+1)}. \quad (\text{C.9})$$

²⁶ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 75.

²⁷ Reference 26, pp. 38–39.

²⁸ Reference 26, p. 223.