interest to note that electron diffraction[17] has given a value of 0.95±0.07A for the nitrogen hydrogen separation in NH_4Cl at room temperature.) Interpretations in terms of stationary tetrahedra involving angular displacement disorder are much less likely.

The disappearance of the piezoelectric effect and the absence or weakening of the Raman line, 183 cm^{-1}, above $-30°C$ can now no longer be explained in terms of disorder or a centro-symmetric structure. However, angular oscillations of the ammonium tetrahedra may disturb the charge distribution in the lattice sufficiently to weaken the Raman line and to make the piezoelectric effect unobservable. A sudden onset of such oscillations may also be the cause of the lattice expansion at the transition temperature and the discontinuity in specific heat.

Theoretical studies are being undertaken to explain the observed behavior, and further experiments are planned to study as a function of temperature the change from the $-180°C$ form to the room temperature form. This is of particular interest because of the existence of a magnetic resonance line width transition at $-140°C$.[30]

We wish to thank Dr. N. K. Pope for his help and advice regarding the theoretical aspects of the work, and Mr. W. J. Woytowich for his technical assistance.

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[30] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 16, 1164 (1948).

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The Theory of Pressure Broadening and Its Application to Microwave Spectra

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In this paper the calculation of the widths of several absorption lines in the microwave region is attempted. First, the fourier integral formula for transition probability is deduced with the adiabatic assumption. Then the width and the shift of the absorption line are calculated, assuming the well type and the inverse power intermolecular potential. Applying the latter model, the width is calculated for several kinds of self-broadened microwave absorption line. A theoretical formula which gives the width of the ammonia inversion line is obtained as a function of $K/[J(J+1)]^{\frac{1}{2}}$, where K and J are the rotational quantum number. It agrees with experiment for large $K/[J(J+1)]^{\frac{1}{2}}$, and its temperature dependence is also good. In the microwave absorption of oxygen, the quadrupole interaction is shown to be responsible for the width, and our theoretical result agrees with experiment if the quadrupole moment of this molecule is 2.5 to 2.0×10^{-26}. It is also shown that the widths of the rotational lines of linear and symmetric top molecules can be explained by the dipole interaction.

I. INTRODUCTION

It was about half a century ago that the first theory of pressure broadening was proposed by Lorentz.[1] Since then much theoretical and experimental work has been performed on this subject. In microwave spectra, the technique of which has been developed in the past few years, the width can be measured fairly accurately; and recently many interesting data have been obtained in this region. Thus, it may still be interesting and valuable to give further consideration to this subject.

In his theory Lorentz[1] assumed that the molecule is represented by a classical oscillator and that the intermolecular collisions are so strong that the oscillation process is absolutely interrupted by them. His formula which gives the intensity at circular frequency ω is

$$I(\omega)=(c/\pi)[\pi a^2\bar{V}N/\{(\omega-\omega_0)^2+(\pi a^2\bar{V}N)^2\}], \quad (1)$$

where $\bar{V}$ is the mean relative velocity of the molecules, a is the radius of the molecule, N is the number of molecules in unit volume, and c is the total intensity. At $|\omega-\omega_0|=\pi a^2\bar{V}N$ the intensity is just half of the maximum intensity, and thus this quantity gives the half-width of the spectral line. Van Vleck and Weisskopf[2] revised this formula, and Van Vleck and Margenau[3] proved that absorption and emission lines have the same shape in this model. In applying the above formula, the collision radius a was found to be very different from the kinetic collision radius; thus, a was taken as a mere parameter with whose physical meaning we are not concerned.

Kuhn,[4] Margenau,[5] and some others developed a theory in which molecules are assumed to be randomly distributed in space and simultaneously interacting with the radiating molecule. This theory is valid at high pressure and can explain the asymmetry of line shape which is observed in this region. But since we are treating the low pressure region, we cannot use this theory.

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[1] H. A. Lorentz, Proc. Amst. Acad. Sci. 8, 591 (1906).

[2] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. 17, 227 (1945).

[3] J. H. Van Vleck and H. Margenau, Phys. Rev. 76, 1211 (1949).

[4] H. Kuhn, Proc. Roy. Soc. (London) A18, 987 (1934).

[5] H. Margenau, Phys. Rev. 48, 755 (1935); H. Margenau and W. W. Watson, Revs. Modern Phys. 8, 22 (1936).

Another theory, called the fourier integral theory, was developed by Weisskopf.[6] By the WKB method he obtained the following formula:

$$I(\omega)\propto\left|\int^{\infty}\exp\left\{-i\omega_0 t-i\int^{t}(\Delta p/\hbar)dt+i\omega t\right\}dt\right|^2,\qquad(2)$$

where Δp is the difference of the intermolecular forces in initial and final states of the radiating process. Lindholm,[7] Foley,[8] and Anderson[9] have recently developed theories of this type, and the present author[10–12] has also published some papers in this direction. In this paper we shall use the fourier integral theory.

II. DISCUSSION ON THE FOURIER INTEGRAL THEORY

The simultaneous collisions of three or more molecules are neglected throughout this paper because we are treating the extremely low pressure region.

The hamiltonian of a two-molecular system can be divided into three parts:

$$H=H_\alpha+H_\beta+H_{\alpha\beta},\qquad(3)$$

where H_α and H_β are the hamiltonians of the isolated molecules α and β, respectively, and $H_{\alpha\beta}$ is the intermolecular potential between these two molecules. If the radiation field interacts with molecule α, H_r must be added to the above hamiltonian, where

$$H_r=F\mu e^{i\omega t},\qquad(4)$$

μ is the dipole moment of molecule α, ω is the circular frequency of the field, and F is the amplitude. Since we do not take into account the simultaneous optical transition of two molecules, we do not need the hamiltonian which gives the interaction of the radiation field with molecule β. In this paper α is called the radiating molecule, and β is called the colliding molecule.

In the radiation theory it is convenient to take the basis which makes H_α and H_β diagonal. In this case the Schroedinger equation is

$$i\hbar\partial a_2^*/\partial t=\textstyle\sum_i(H-i\hbar\partial/\partial t)_{2i}a_i^*,\qquad(5)$$

where a_i^* is the probability amplitude of state i. The term $i\hbar\partial/\partial t$ comes from the relative motion of the molecules.[12a] In the following we shall restrict ourselves to the adiabatic case; that is, we shall neglect the effect of the motion of the molecule. The adiabatic assumption in Eq. (5) means neglecting $i\hbar\partial/\partial t$ as compared with H. In this case we obtain

$$i\hbar\dot{a}_2^*=(E_2+v_2)a_2^*+\textstyle\sum_i(H_{\alpha\beta}''+H_r)_{2i}a_i^*,\qquad(6)$$

where $\dot{a}_2^*$ is the time derivative of a_2^*, E_2 is the energy of the isolated molecule in state 2, v_2 is the eigenvalue of the diagonal part of $H_{\alpha\beta}$, and $H_{\alpha\beta}''$ is the remaining part of $H_{\alpha\beta}$. Turning to Heiseberg's representation

$$a_i^*=a_i\exp\left\{-i\left(E_it+\int^t v_idt\right)\Big/\hbar\right\},\qquad(7)$$

and neglecting all a_i except $a_1(=1)$ according to the initial condition, our equation becomes

$$i\hbar\dot{a}_2=(H_{\alpha\beta}''+H_r)_{21}\times\exp\left[i\left\{(E_2-E_1)t+\int^t(v_2-v_1)dt\right\}\Big/\hbar\right].\qquad(8)$$

If we neglect $H_{\alpha\beta}''$, the transition probability from 1 to 2 is obtained by integration to be

$$\mu_{21}{}^2F^2\left|\int^{\infty}\exp\left[i\left\{(E_2-E_1)t+\int^t(v_2-v_1)dt\right\}\Big/\hbar+i\omega t\right]dt\right|^2,\qquad(9)$$

which is the fourier integral formula.

This procedure is generalized to include nondiagonal terms as follows. Taking the same basis as above, our Schroedinger equation in matrix form is

$$i\hbar\partial\mathbf{a}^*/\partial t=(\mathbf{H}_\alpha+\mathbf{H}_\beta+\mathbf{H}_{\alpha\beta}+\mathbf{H}_r)\mathbf{a}^*.\qquad(10)$$

By a unitary transformation $\mathbf{T}$, $(\mathbf{H}_\alpha+\mathbf{H}_\beta+\mathbf{H}_{\alpha\beta})$ is diagonalized.

$$\mathbf{T}(\mathbf{H}_\alpha+\mathbf{H}_\beta+\mathbf{H}_{\alpha\beta})\mathbf{T}^{-1}=(V_i\delta_{ij}).\qquad(11)$$

Transforming by $\mathbf{T}$, Eq. (10) becomes

$$\begin{aligned}i\hbar\mathbf{T}\partial\mathbf{a}/\partial t^*\mathbf{T}^{-1}&=\mathbf{T}(\mathbf{H}_\alpha+\mathbf{H}_\beta+\mathbf{H}_{\alpha\beta}+\mathbf{H}_r)\mathbf{T}^{-1}\mathbf{T}\mathbf{a}^*\mathbf{T}^{-1}\\&=\{(V_i\delta_{ij})+\mathbf{T}\mathbf{H}_r\mathbf{T}^{-1}\}\mathbf{T}\mathbf{a}^*\mathbf{T}^{-1}.\end{aligned}\qquad(12)$$

Then, by a transformation analogous to Eq. (7), and neglecting $\partial\mathbf{T}/\partial t$ by the adiabatic assumption, we get

$$\begin{aligned}i\hbar\mathbf{T}\partial\mathbf{a}/\partial t\mathbf{T}^{-1}=&\left\{\exp\left(i\int^t V_idt\Big/\hbar\right)\delta_{ij}\right\}\mathbf{T}\mathbf{H}_r\mathbf{T}^{-1}\\&\times\left\{\exp\left(-i\int^t V_idt\Big/\hbar\right)\delta_{ij}\right\}\mathbf{T}\mathbf{a}\mathbf{T}^{-1}.\end{aligned}\qquad(13)$$

Finally, by the inverse transformation,

$$\begin{aligned}i\hbar\partial\mathbf{a}/\partial t=\mathbf{T}^{-1}&\left\{\exp\left(i\int^t V_idt\Big/\hbar\right)\delta_{ij}\right\}\mathbf{T}Fe^{i\omega t}\boldsymbol{\mu}\mathbf{T}^{-1}\\&\times\left\{\exp\left(-i\int^t V_idt\Big/\hbar\right)\delta_{ij}\right\}\mathbf{T}\mathbf{a}.\end{aligned}\qquad(14)$$

When integrated this gives the generalized fourier integral formula.

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[6] V. F. Weisskopf, Physik. Z. **34**, 1 (1933).

[7] E. Lindholm, Arkiv. Mat. Astron. Fysik. **32**, 17 (1945).

[8] H. M. Foley, Phys. Rev. **69**, 616 (1946).

[9] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[10] M. Mizushima, Phys. Rev. **74**, 705 (1946).

[11] M. Mizushima, J. Phys. Soc. Japan **4**, 191 (1949).

[12] M. Mizushima, Research Chem. Phys. **29**, 25 (1950).

[12a] That the term $i\hbar\partial/\partial t$ must be included in the right side of this equation was first pointed out by H. Margenau (private communication).

In cases where the intermolecular potential is so small that it can be taken into account by the second-order perturbation, the matrix **T** is approximated by the unit matrix. In this case

$$i\hbar\dot{a}_i = F\mu_{ij}\exp\left[i\left\{(E_i-E_j)t + \int^t (v_i'-v_j')dt\right\}\Big/\hbar + i\omega t\right]a_j, \quad (15)$$

where

$$V_i = E_i + v_i'.$$

By integration, Weisskopf's formula (2) is obtained.

Foley[8] has proved that Weisskopf's formula can be reduced to

$$I(\omega) = (c/\pi)[(A/\tau_0)/\{(\omega-\omega_0-B/\tau_0)^2+(A/\tau_0)^2\}], \quad (16)$$

where

$$A = \langle 1-\cos\alpha\rangle_{\text{Av}}, \quad B = \langle\sin\alpha\rangle_{\text{Av}}, \quad \alpha = \int(\Delta p/\hbar)dt,$$

and τ_0 is the mean time between collisions. His derivation of Eq. (16) is inadequate in that he replaced the sum of averages by the average of sums [Eqs. (14) and (15) in reference 8], although the recalculation with corrected order does not change the result essentially. Doing this, and avoiding the use of τ_0, we can easily obtain

$$I(\nu) = (c/\pi)[\Delta\nu/\{(\nu-\nu_0-\Delta\nu')^2+(\Delta\nu)^2\}], \quad (17)$$

which corresponds to Eq. (16), where

$$\Delta\nu = \int F(s)(1-\cos\alpha_s)ds/2\pi, \quad (18a)$$

$$\Delta\nu' = \int F(s)\sin\alpha_s ds/2\pi. \quad (18b)$$

and $F(s)ds$ is the number of collisions with collision parameters between s and $s+ds$ in unit time. In Eq. (17), $\Delta\nu$ is usually called the width parameter, and $\Delta\nu'$ gives the shift of intensity maximum by pressure.

In the case of an absorption line, to which the present consideration is limited, $F(s)ds$ can be obtained by the gas kinetic theory as

$$F(s)ds = 8\pi^{\frac{1}{2}}(m/2kT)^{\frac{3}{2}} \times\exp(-mV^2/2kT)V^3dV\rho d\rho GN, \quad (19)$$

where m is the reduced mass, V is the relative velocity, ρ is the impact parameter of collision, G is the probability of the molecule being in a rotational state, and N is the number of molecules in unit volume. In Eq. (19), V and ρ are integrated from 0 to ∞, and G is summed over all states.

III. WELL-TYPE POTENTIAL AND THE LORENTZ FORMULA

If the intermolecular potential is such that

$$\Delta p = \gamma \text{ for } R<a, \quad \Delta p = 0 \text{ for } R>a, \quad (20)$$

then the integral α is

$$\alpha = 2(a^2-\rho^2)^{\frac{1}{2}}\gamma/(V\hbar). \quad (21)$$

Thus our formulas (18) give

$$\Delta\nu = \tfrac{1}{2}a^2\bar{V}N - 4\pi^{-\frac{1}{2}}\hbar^2(m/4kT)^{\frac{3}{2}}\int_0^\infty \varphi^{-8} \times\exp(-m/4kT\varphi^2)\{(a\varphi/2\gamma\hbar)\sin(2\gamma a\varphi/\hbar) + [\cos(2\gamma a\varphi/\hbar)-1]/4\gamma^2\}d\varphi, \quad (22a)$$

$$\Delta\nu' = 4\pi^{-\frac{1}{2}}\hbar^2(m/4kT)^{\frac{3}{2}}\int_0^\infty \varphi^{-8}\exp(-m/4kT\varphi^2) \times\{\sin(2\gamma a\varphi/\hbar)/4\gamma^2 - (a\varphi/2\gamma\hbar)\cos(2\gamma a\varphi/\hbar)\}d\varphi, \quad (22b)$$

respectively.

If the potential difference is so large that we may put $\gamma=\infty$, then we obtain Lorentz's formulas:

$$\Delta\nu = a^2\bar{V}N/2, \quad (23a)$$

$$\Delta\nu' = 0. \quad (23b)$$

Thus, we can make an interpretation of the so-called strong collision in the present theory.

V. INVERSE POWER POTENTIAL

There are many cases where Δp can be expressed as

$$\Delta p = \hbar\Delta\mu/R^n, \quad (24)$$

where R is the intermolecular distance. If the path of the molecule is straight, then by Eq. (16),

$$\alpha = \int_{-\infty}^{\infty}\Delta\mu/(\rho^2+V^2t^2)^{n/2}dt = (\Delta\mu/V\rho^{n-1})\pi\Gamma(n-1)2^{2-n}[\Gamma(n/2)]^{-2}. \quad (25)$$

Thus, our formulas which give the width and the shift of a spectral line become

$$\Delta\nu = (\pi^{(5-n)/(2n-2)}/2)(kT/2m)^{(3-n)/(2n-2)} \times\Gamma((2n-3)/(n-1))\Gamma((n-3)/(n-1)) \times[\Gamma(n-1)/\{\Gamma(n/2)\}^2]^{2/(n-1)} \times\sin\{\pi(n-3)/(2n-2)\}\langle|\Delta\mu|^{2/(n-1)}\rangle N, \quad (26a)$$

$$\Delta\nu' = \tan[\pi/(n-1)]\Delta\nu\langle\Delta\mu/|\Delta\mu|\rangle, \quad (26b)$$

where n must be larger than 2; otherwise they diverge.

For some special values of n, which we shall meet later, these equations give

$$\Delta\nu=(\pi/2)\langle|\Delta\mu|\rangle N \text{ for } n=3, \tag{27a}$$

$$\Delta\nu=(2/\sqrt{3})\Gamma(7/4)(kT/M)^{1/4}\langle|\Delta\mu|^{\frac{1}{2}}\rangle N \text{ for } n=5, \tag{27b}$$

$$\begin{aligned}\Delta\nu=&(\pi^{-1/10}/2)(kT/M)^{3/10}\Gamma(9/5)\Gamma(3/5)\\ &\times\{12/\Gamma(3)\}^{2/5}\sin(3\pi/10)\langle|\Delta\mu|^{2/5}\rangle N\\ &\text{for } n=6,\end{aligned} \tag{27c}$$

respectively. (In these formulas the real mass $M=2m$ is used.) The last formula agrees approximately with that of Lindholm.[7] We do not calculate the shift except for some simple cases.

If the sign of $\Delta\mu$ is common to all collisions, Eq. (26) gives Foley's relation[8]

$$|\Delta\nu'|/\Delta\nu=\tan[\pi/(n-1)]. \tag{28}$$

But in most cases of molecular spectra the above assumption does not hold, and Eq. (28) cannot be applied.

In the case of molecules, $\Delta\mu$ contains some factors which depend on angular variables. If the orientation of the molecule in space does not change in a collision, these factors may also vary with R. We shall neglect this effect throughout this paper; that is, we assume the orientation to change suitably in a collision.

VI. INVERSION SPECTRUM OF AMMONIA

There has been much theoretical and experimental work on this famous microwave absorption spectrum. The measurement of the width by Bleaney and Penrose[13] showed an interesting regularity, which we shall consider in this section. The theoretical calculation of the width was first attempted by the present author.[10,11] In these papers he succeeded in explaining Good's experimental result.[14] Margenau[15] showed by a simple calculation that the width parameter for each J, K line can be expressed by

$$\Delta\nu=34K/[J(J+1)]^{\frac{1}{2}} \text{ Mc/mm Hg}, \tag{29}$$

which agrees with the experimental result of Bleaney and Penrose. Anderson,[9] making an elaborate theoretical consideration, succeeded in explaining the relative width of these fine structure lines.

The vibrational ground state of the ammonia molecule splits into two states which are symmetric and antisymmetric with respect to the inversion. The wave functions of them are denoted by ψ_+ and ψ_-, respectively.[16]

In the two-molecule system there are four states, whose wave functions are $\psi_+(1)\psi_+(2)$, $\psi_-(1)\psi_-(2)$, $\psi_+(1)\psi_-(2)$, and $\psi_-(1)\psi_+(2)$. The rotational part may be taken into account by simply multiplying them by $\Theta_{J,K,M}(1)\Theta_{J',K',M'}(2)$, where Θ is the rotational wave function of the symmetric top rotator, and J, K, M are the rotational quantum numbers. Thus, our total wave function is

$$\begin{aligned}&\Psi_{J,K,J,'K'}\\ &=\sum_{M,M'}a_{MM'}\psi_+(1)\Theta_{J,K,M}(1)\psi_+(2)\Theta_{J,'K,'M'}(2)\\ &+\sum_{M,M'}b_{MM'}\psi_-(1)\Theta_{J,K,M}(1)\psi_-(2)\Theta_{J,'K,'M'}(2)\\ &\quad+\sum_{MM'}c_{MM'}\psi_+(1)\Theta_{J,K,M}(1)\psi_-(2)\Theta_{J,'K,'M'}(2)\\ &\quad+\sum_{M,M'}d_{MM'}\psi_-(1)\Theta_{J,K,M}(1)\psi_+(2)\Theta_{J,'K,'M'}(2).\end{aligned} \tag{30}$$

The main part of the intermolecular potential is the dipole-dipole interaction

$$H_{\alpha\beta}=\{\boldsymbol{\mu}_\alpha\cdot\boldsymbol{\mu}_\beta-3(\boldsymbol{\mu}_\alpha\cdot\mathbf{R})(\boldsymbol{\mu}_\beta\cdot\mathbf{R})/R^2\}/R^3. \tag{31}$$

Thus our matrix $\mathbf{H}_{\alpha\beta}$

$$\mathbf{H}_{\alpha\beta}=\begin{bmatrix}-\epsilon\mathbf{E} & \mathbf{A} & 0 & 0\\ \mathbf{A} & \epsilon\mathbf{E} & 0 & 0\\ 0 & 0 & 0 & \mathbf{A}\\ 0 & 0 & \mathbf{A} & 0\end{bmatrix}, \tag{32}$$

where ϵ is the energy difference of ψ_+ and ψ_- states of an isolated molecule and $\mathbf{A}$ is the matrix obtained by Margenau and Warren,[17]

$$\begin{aligned}&(M_jM_j'|A|M_iM_i')\\ &=(\mu^2/R^3)\{KK'/[J(J+1)J'(J'+1)]\}\\ &\qquad\times[-2M_iM_i'\delta(M_j,M_i)\delta(M_j',M_i')\\ &\qquad\pm\tfrac{1}{2}\{(J-M_i+1)(J+M_i)(J'-M_i')(J'+M_i'+1)\}^{\frac{1}{2}}\\ &\qquad\times\delta(M_j,M_i-1)\delta(M_j',M_i'+1)\\ &\qquad\pm\tfrac{1}{2}\{(J+M_i+1)(J-M_i)(J'+M_i')(J'-M_i'+1)\}^{\frac{1}{2}}\\ &\qquad\qquad\qquad\times\delta(M_j,M_i+1)\delta(M_j',M_i'-1)].\end{aligned} \tag{33}$$

If $\mathbf{l}$ is a transformation matrix which diagonalizes $\mathbf{A}$, then $\mathbf{L}=\mathbf{l}+\mathbf{l}+\mathbf{l}+\mathbf{l}$ (direct sum) transforms our matrix (32) to

$$\mathbf{L}\mathbf{H}_{\alpha\beta}\mathbf{L}^{-1}=\begin{bmatrix}-\epsilon\mathbf{E} & (e_i\delta_{ij}) & 0 & 0\\ (e_i\delta_{ij}) & \epsilon\mathbf{E} & 0 & 0\\ 0 & 0 & 0 & (e_i\delta_{ij})\\ 0 & 0 & (e_i\delta_{ij}) & 0\end{bmatrix}, \tag{34}$$

which can be factorized easily. Thus it is shown that the following four-dimensional reduced matrix is sufficient for our calculation;

$${}_m\mathbf{H}_{\alpha\beta}=\begin{bmatrix}-\epsilon & e_m & 0 & 0\\ e_m & \epsilon & 0 & 0\\ 0 & 0 & 0 & e_m\\ 0 & 0 & e_m & 0\end{bmatrix},\quad m=1,\cdots,(2J+1)(2J'+1). \tag{35}$$

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[13] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) 59, 424 (1947).

[14] W. Good, Phys. Rev. 70, 213 (1946).

[15] H. Margenau, Phys. Rev. 76, 121 (1949).

[16] G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

[17] H. Margenau and D. J. Warren, Phys. Rev. 51, 748 (1935).

The unitary matrix which diagonalizes this matrix is

$$ {}_m\mathbf{T}=\begin{bmatrix} a & -b & 0 & 0 \\ b & a & 0 & 0 \\ 0 & 0 & 2^{-\frac{1}{2}} & -2^{-\frac{1}{2}} \\ 0 & 0 & 2^{-\frac{1}{2}} & 2^{-\frac{1}{2}} \end{bmatrix}, \tag{36}$$

$$a=\{(\epsilon^2+e_m^2)^{\frac{1}{2}}+\epsilon\}^{\frac{1}{2}}/(4\epsilon^2+4e_m^2)^{\frac{1}{4}},$$

$$b=\{(\epsilon^2+e_m^2)^{\frac{1}{2}}-\epsilon\}^{\frac{1}{2}}/(4\epsilon^2+4e_m^2)^{\frac{1}{4}},$$

and[18]

$$ {}_m\mathbf{T}_m\mathbf{H}_{\alpha\beta m}\mathbf{T}^{-1}=\begin{bmatrix} -(\epsilon^2+e_m^2)^{\frac{1}{2}} & 0 & 0 & 0 \\ 0 & (\epsilon^2+e_m^2)^{\frac{1}{2}} & 0 & 0 \\ 0 & 0 & -e_m & 0 \\ 0 & 0 & 0 & e_m \end{bmatrix}. \tag{37}$$

From symmetry considerations, it is clear that

$$\int \psi_+\mu\psi_+d\tau=\int \psi_-\mu\psi_-d\tau=0, \tag{38}$$

and it was shown[19] that

$$\int \psi_+\mu\psi_-d\tau=\mu^* \tag{39}$$

is the quantity obtained by the dielectric constant measurement as the dipole moment of this molecule. Thus our matrix $\boldsymbol{\mu}$ is

$$\boldsymbol{\mu}=\mu^*\begin{bmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{bmatrix}. \tag{40}$$

From Eqs. (13), (36), (37), and (40), we obtain the following formula

$$\begin{bmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \dot{a}_3 \\ \dot{a}_4 \end{bmatrix}=\mu^*Fe^{i\omega t}\begin{bmatrix} 0 & 0 & c^* & c^* \\ 0 & 0 & c^* & c^* \\ c & c & 0 & 0 \\ c & c & 0 & 0 \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix}, \tag{41}$$

where

$$c=\Big[\{(\epsilon^2+e_m^2)^{\frac{1}{2}}+\epsilon-e_m\}\times\exp\Big\{i\int^t([e_m+(\epsilon^2+e_m^2)^{\frac{1}{2}}]/\hbar)dt\Big\}+\{(\epsilon^2+e_m^2)^{\frac{1}{2}}-\epsilon+e_m\}\times\exp\Big\{i\int^t([e_m-(\epsilon^2+e_m^2)^{\frac{1}{2}}]/\hbar)dt\Big\}\Big]\Big/(4\epsilon^2+4e_m^2)^{\frac{1}{2}},$$

and c^* is the complex conjugate of c.

Since e_m is an eigenvalue of the matrix (33), it is proportional to R^{-3}. Thus, when the intermolecular distance is smaller than some critical length, e_m is larger than ϵ. In this region, neglecting ϵ as compared with e_m, c can be approximated by

$$c\simeq\exp\Big\{i\int^t(e_m-|e_m|)\hbar^{-1}dt\Big\}. \tag{42}$$

When the intermolecular distance is larger than this critical length, and accordingly $e_m<\epsilon$, the approximate expression for c is

$$c\simeq\exp(i\epsilon t/\hbar). \tag{43}$$

Thus, we use

$$c\simeq\exp\Big\{i\int^t(\epsilon+e_m-|e_m|)\hbar^{-1}dt\Big\} \tag{44}$$

as an approximation throughout these regions.

Putting

$$e_m=\hbar\Delta\mu_m/R^3, \tag{45}$$

we obtain from Eq. (27a) the following formula for the width parameter

$$\Delta\nu_1=(\pi/2)\langle|\Delta\mu_m|-\Delta\mu_m\rangle N. \tag{46}$$

Since Margenau and Warren[17] showed that $\langle\Delta\mu_m\rangle=0$,

$$\Delta\nu_1=(\pi/2)\langle|\Delta\mu_m|\rangle N. \tag{47}$$

Assuming the gaussian distribution for $\Delta\mu_m$, the average may be calculated by using the root mean square of e_m given by Margenau and Warren.[17] Thus,

$$\Delta\nu_1=(\pi/3)^{\frac{1}{2}}(\mu^{*2}/\hbar)\langle|K|/[J(J+1)]^{\frac{1}{2}}\rangle\times|K/[J(J+1)]^{\frac{1}{2}}|N. \tag{48}$$

Numerical calculations were made with $T=297°\mathrm{K}$ and $\mu^*=1.44\times10^{-18}$, and the result is

$$\Delta\nu_1=39|K/[J(J+1)]^{\frac{1}{2}}|\ \mathrm{Mc/mm\ Hg}, \tag{49}$$

which is nearly the same as Margenau's result (29), although the method of calculation is very different.

Approximation (44) is not good at large distances, the actual intermolecular potential being much smaller when $\epsilon>e_m$. Thus, the next approximation is to cut the intermolecular potential at $R_c=(\hbar\Delta\mu_m/\epsilon)^{\frac{1}{3}}$. Using the same α as in the above calculation, but limiting the integration over ρ to $0-R_c$ instead of $0-\infty$, we easily obtain the following formula

$$\Delta\nu_2=\Delta\nu_1-8(2\pi/3)^{\frac{1}{2}}(M/4kT)^{\frac{1}{2}}\epsilon^{\frac{2}{3}}\hbar^{-2}\times\mu^{*8/3}\langle|K/[J(J+1)]^{\frac{1}{2}}|^{4/3}\rangle\times|K/[J(J+1)]^{\frac{1}{2}}|^{4/3}N, \tag{50}$$

which, at 297°K, is

$$\Delta\nu_2=39|K/[J(J+1)]^{\frac{1}{2}}|-13|K/[J(J+1)]^{\frac{1}{2}}|^{4/3}\ \mathrm{Mc/mm\ Hg}. \tag{51}$$

These formulas are plotted in Fig. 1 together with the experimental data of Bleaney and Penrose.[13] We see that our formula (51) agrees very well with experi-

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[18] This result was published independently by the present author (references 10 and 11) and Margenau [H. Margenau, Phys. Rev. **76**, 1423 (1949)].

[19] M. Mizushima, J. Phys. Soc. Japan 4, 11 (1949).

ment at large values of $K/[J(J+1)]^{\frac{1}{2}}$. It is quite natural that the agreement is not so good for small values of $K/[J(J+1)]^{\frac{1}{2}}$, since in that region the second-order force, which is not considered in this paper, may contribute a great deal.

Howard and Smith[20] measured the width of the 3,3 line at 300°K and 195°K, and found that the width is larger at the lower temperature. The ratio of the widths at these two temperatures at constant pressure is 0.66 ± 0.03. Our theory predicts that

$$\Delta\nu_2=59.5|K/[J(J+1)]^{\frac{1}{2}}|-22|K/[J(J+1)]^{\frac{1}{2}}|^{4/3}\ \text{Mc/mm Hg} \quad (52)$$

at 195°K. The ratio of Eq. (51) to Eq. (52) for the 3,3 line is 0.69, which agrees very well with the above experimental result.[21]

From $\langle\Delta\mu_m\rangle=0$ we can easily conclude that the shift of the line is zero.

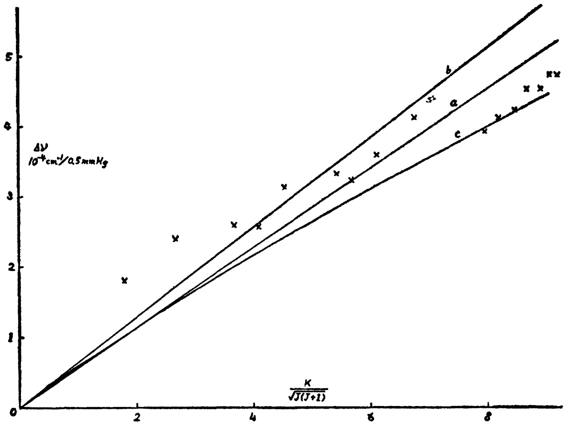

FIG. 1. Width parameters of ammonia inversion lines. x, Bleaney and Penrose's experimental results (reference 13); a, Margenau's theoretical curve [Eq. (29)]; b, Eq. (49); c, Eq. (51).

VII. MAGNETIC ABSORPTION OF OXYGEN

Since the electronic ground state of oxygen is $^3\Sigma$, this molecule has a magnetic absorption in the microwave region, corresponding to transitions among the triplet levels. Beringer[22] observed this absorption first, and Van Vleck[23] made a theoretical consideration of it, taking the width as merely a parameter. Later, Strandberg *et al.*,[24] and Beringer and Castle[25] measured this absorption, but they could not succeed in separating the fine structure. Recently, Gordy *et al.*[26] have finally succeeded in observing the fine structure, and they have also observed the widths of some lines.[27]

In this molecule, the total angular momentum **J** is composed of the electronic spin angular momentum **S** ($|\mathbf{S}|=1$), and the ordinary rotational one **K**. Thus, there are three states $J=K+1$, K, $K-1$ corresponding to one K, except for $K=0$, 1 states. The wave functions of these three states are obtained[28] as

$$\begin{pmatrix}\Psi_{K+1,M}\\ \\ \Psi_{K,M}\\ \\ \Psi_{K-1,M}\end{pmatrix}=\begin{pmatrix}\left\{\dfrac{(K+M)(K+M+1)}{2(2K+1)(K+1)}\right\}^{\frac{1}{2}} & \left\{\dfrac{(K-M+1)(K+M+1)}{(2K+1)(K+1)}\right\}^{\frac{1}{2}} & \left\{\dfrac{(K-M)(K-M+1)}{2(2K+1)(K+1)}\right\}^{\frac{1}{2}}\\ \left\{\dfrac{(K+M)(K-M+1)}{2K(K+1)}\right\}^{\frac{1}{2}} & \dfrac{M}{\{K(K+1)\}^{\frac{1}{2}}} & \left\{\dfrac{(K-M)(K+M+1)}{2K(K+1)}\right\}^{\frac{1}{2}}\\ \left\{\dfrac{(K-M)(K-M+1)}{2K(2K+1)}\right\}^{\frac{1}{2}} & \left\{\dfrac{(K-M)(K+M)}{K(2K+1)}\right\}^{\frac{1}{2}} & \left\{\dfrac{(K+M+1)(K+M)}{2K(2K+1)}\right\}^{\frac{1}{2}}\end{pmatrix}\begin{pmatrix}\Theta_{K,M-1}\sigma_1\\ \\ \Theta_{K,M}\sigma_0\\ \\ \Theta_{K,M+1}\sigma_{-1}\end{pmatrix}, \quad (53)$$

where $\Theta_{K,M}$ is the ordinary rotational wave function of a linear molecule with quantum numbers K, M; σ_m is the spin wave function, and m is its magnetic quantum number.

The energies of these three states were calculated by Kramers[29] and Schlapp;[30] but, according to Gordy *et al.*,[27] their theoretical results may be revised in some respects. Anyway, it is known that $J=K$ is the highest level, and the other two levels are a little lower and near to each other. The separations of these levels depend on K.

Magnetic absorption is allowed for $J=K-1\rightarrow K$ and $J=K+1\rightarrow K$ transitions, and thus there are two kinds of absorption lines.

There are no dipole forces between oxygen molecules. The contribution to the width by the London force seems to be small, since $K\pm1$ and K states have nearly common electronic states and the London force is nearly equal for these states.[30a] Of course, there is the magnetic dipole interaction between oxygen molecules, but this is found to be so small that it cannot explain the observed width. We shall try to calculate the width due

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[20] R. Howard and W. V. Smith, Phys. Rev. **77**, 840 (1950).

[21] Anderson's theory (reference 9) could also explain the same experiment (reference 21). However, the agreement of the two theoretical results in this case is rather accidental. The temperature dependence of other lines may distinguish between these two theories.

[22] R. Beringer, Phys. Rev. **70**, 53 (1946).

[23] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947).

[24] Strandberg, Meng, and Ingersoll, Phys. Rev. **75**, 1524 (1949).

[25] R. Beringer and J. G. Castle, Phys. Rev. **75**, 1963 (1949).

[26] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **77**, 152 (1950).

[27] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **79**, 651 (1950).

[28] See E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 76.

[29] H. A. Kamers, Z. Physik **53**, 422 (1929).

[30] R. Schlapp, Phys. Rev. **51**, 342 (1937).

[30a] The contribution by this force was estimated by H. Margenau (private communication).

TABLE I. Width of oxygen lines.

K	3	13	21
Species	$K-1\rightarrow K$	$K+1\rightarrow K$	$K-1\rightarrow K$
$\Delta\nu$ (Mc/mm Hg)	2.1	0.87	0.83

to the electric quadrupole moment in the following paragraphs.

The diagonal element of the quadrupole interaction between two linear molecules is known to be[31]

$$\int \Theta_{K,M}^2(1)\Theta_{K',M'}^2(2)V_{12}d\tau$$
$$=(6Q^2/R^5)[\{K(K+1)-3M^2\}/(2K+3)(2K-1)]$$
$$\times[\{K'(K'+1)-3M'^2\}/(2K'+3)(2K'-1)], \quad (54)$$

where Q is the quadrupole moment. Since it is suitably factored, we can calculate it separately for each molecule.

Using the wave functions (53), we can calculate the diagonal element of the quadrupole interaction between two oxygen molecules. The factor which comes from one molecule is

$$K\{(K+1)(K+2)-3M^2\}/\{(2K+1)(K+1)(2K+3)\} \quad \text{for } J=K+1, \quad (55a)$$

$$\{K(K+1)-3\}\{K(K+1)-3M^2\}/\{K(K+1)(2K+3)(2K-1)\} \quad \text{for } J=K, \quad (55b)$$

$$(K+1)\{K(K-1)-3M^2\}/\{K(2K+1)(2K-1)\} \quad \text{for } J=K-1. \quad (55c)$$

This interaction being proportional to R^{-5}, we use Eq. (27b) to calculate the width parameter, and thus the average of the square root of the potential difference is required. In calculating the mean value for the colliding molecules, all of Eqs. (55) may be replaced by a single expression

$$(K^2-3M^2)/4K^2, \quad (56)$$

since the mean K is very large at room temperature. The mean root of Eq. (56) is

$$(1/2K)^2\left\{\int_0^{K/\sqrt{3}}(K^2-3M^2)^{\frac{1}{2}}dM + \int_{K/\sqrt{3}}^{K}(3M^2-K^2)^{\frac{1}{2}}dM\right\}=0.254\cdots, \quad (57)$$

which does not depend on K. Thus,

$$\Delta\nu=(0.254)2^{\frac{3}{4}}\Gamma(7/4)(kT/M)^{\frac{1}{4}}Q\hbar^{-\frac{1}{2}}\langle|A|\rangle N, \quad (58)$$

where

$$A=(55a)-(55b) \quad \text{for } K+1\rightarrow K,$$
$$A=(55c)-(55b) \quad \text{for } K-1\rightarrow K.$$

For simplicity, we shall limit our consideration here to the case of $M=M'$.

Gordy's experimental results[27] are shown in Table I. We see in this table that the width decreases as K increases and that the $K+1\rightarrow K$ line is a little broader than the $K-1\rightarrow K$ line.

For $K=3$, the calculation may be performed numerically, the results being

$$\Delta\nu=8.6\times10^{25}Q \text{ Mc/mm Hg} \quad \text{for } K+1\rightarrow K, \quad (59a)$$

$$\Delta\nu=8.4\times10^{25}Q \text{ Mc/mm Hg} \quad \text{for } K-1\rightarrow K, \quad (59b)$$

at room temperature.

In order to explain the experimental result of Gordy, Q must be 2.5×10^{-26}. Although there is no direct measurement of Q, we know that the experimental curve of Lassettre and Dean[32] for molecules with single bonds predicts for a fictitious molecule with a single bond of the same internuclear distance as oxygen, $Q=3.4\times10^{-26}$; and for the pressure absorption of this molecule, a somewhat lower value is required.[33] Thus our value of Q may be said to be of a plausible order.

For large K, expanding A in powers of $1/K$, we obtain

$$\Delta\nu=(1.84\times10^{26}Q/K^{\frac{1}{2}})[1-(3/8K)+\cdots] \quad \text{for } K+1\rightarrow K, \quad (60a)$$

$$\Delta\nu=(1.84\times10^{26}Q/K^{\frac{1}{2}})[1+(3/8K)+\cdots] \quad \text{for } K-1\rightarrow K. \quad (60b)$$

Thus we can see that the width parameter decrease as K increases, in agreement with the experimental result. In these formulas the coefficients of the second terms in parentheses are not certain, but they make the $K+1\rightarrow K$ line narrower than the $K-1\rightarrow K$ line. The calculated width parameters for the other two lines in the table are 1.24 and 1.00 Mc/mm Hg for the $13+1\rightarrow13$ and $21-1\rightarrow21$ lines, respectively, if $Q=2.5\times10^{-26}$. They are near to the experimental values, but too large.*

Recently, Beringer and Castle[34] have observed the magnetic resonance spectrum of oxygen, and measured the widths of some lines. Since in their case the transition is different from the kind discussed above, our theory cannot be applied directly.[34a] However, if their width is due to the electric quadrupole moment as is assumed in this paper, its temperature dependence may be predicted by Eq. (27b), that is,

$$\Delta\nu\propto T^{-\frac{3}{4}} \text{ at constant pressure.}$$

It is interesting that Beringer and Castle's experi-

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[31] H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

[32] E. N. Lassettre and L. B. Dean, Jr., J. Chem. Phys. **17**, 317 (1949).

[33] M. Mizushima, Phys. Rev. **76**, 1268 (1949); **77**, 149 (1950).

* *Note added in proof:* Recently, R. S. Anderson, W. V. Smith, and W. Gordy have measured the width of fourteen lines from $K=1$ to 23 of oxygen. Their results for lines of K larger than 11 agree very well with our $K^{-\frac{1}{2}}$ formula (60). Their new data yield $Q=3.6\times10^{-26}$ (Anderson, Smith, and Gordy, private communication.)

[34] R. Beringer and J. G. Castle, Jr., Phys. Rev. **81**, 82 (1951).

[34a] H. Margenau has made some theoretical calculations on this case (private communication).

mental data at 300°K and 85°K lie midway between the T^{-1} and $T^{-\frac{1}{2}}$ dependences.

VII. THE ROTATIONAL ABSORPTION LINES OF LINEAR MOLECULES

There are many data on this kind of absorption line.[35] In this case, the London force need not be considered, since its contribution may be smaller than that of the dipole interaction. The matrix element of the dipole interaction (31) for a linear molecule is[31]

$$\begin{aligned}(JMJ'M'|V|jmj'm')&\\ =(\mu^2/2R^3)\{&A(-M)A(M')\delta_{m,M-1}\delta_{m',M'+1}\\ &+A(M)A(-M')\delta_{m,M+1}\delta_{m',M'-1}\\ &-2B(M)B(M')\delta_{m,M}\delta_{m',M'}\}.\end{aligned}$$

where

$$\begin{aligned}A(\pm M)&=\left[\frac{(J\pm M+2)(J\pm M+1)}{(2J+3)(2J+1)}\right]^{\frac{1}{2}}\delta_{j,J+1}\\ &\quad-\left[\frac{(J\mp M+1)(J\mp M)}{(2J+1)(2J-1)}\right]^{\frac{1}{2}}\delta_{j,J-1},\\ B(M)&=\left[\frac{(J+M+1)(J-M+1)}{(2J+3)(2J+1)}\right]^{\frac{1}{2}}\delta_{j,J+1}\\ &\quad+\left[\frac{(J+M)(J-M)}{(2J+1)(2J-1)}\right]^{\frac{1}{2}}\delta_{j,J-1}.\end{aligned}\tag{61}$$

London calculated the intermolecular potential by the second-order perturbation method.[31] If it were valid, we could easily calculate the width; but unfortunately this is not the case. At room temperature, the molecules with J values satisfying $\hbar^2J(J+1)/2I=kT\simeq3\times10^{-14}$ erg are most common; that is, $J_{\max}\simeq30$ for $I=10^{-38}$, while the intermolecular potential μ^2/R^3 is about 10^{-14} at 5A. Thus, the latter potential is usually larger than the energy difference of successive rotational states $\hbar^2J/I$. For this reason, we cannot use the second-order perturbation theory; and, on the contrary, an approximation neglecting the diagonal elements may be better.

In the latter approximation, the eigenvalue is proportional to R^{-3}; thus, by Eq. (27a) the mean potential difference is required in calculating the width. By anticipating this, we take the root mean square of the matrix element over M and M' at the beginning, for simplicity. Then our matrix is

$$\begin{aligned}(JJ'|V|jj')=(2/3)^{\frac{1}{2}}(\mu^2/R^3)&\{(2J+1)(2J'+1)\}^{-\frac{1}{2}}\\ &\times\{(J+1)^{\frac{1}{2}}\delta_{j,J+1}+J^{\frac{1}{2}}\delta_{j,J-1}\}\\ &\times\{(J'+1)^{\frac{1}{2}}\delta_{j',J'+1}+J'^{\frac{1}{2}}\delta_{j',J'-1}\}.\end{aligned}\tag{62}$$

Since the rotational quantum number of the colliding molecule is usually very large, Eq. (62) may be approximated by

$$\begin{aligned}(JJ'|V|jj')=3^{-\frac{1}{2}}&(\mu^2/R^3)(2J+1)^{-\frac{1}{2}}\\ &\times\{(J+1)^{\frac{1}{2}}\delta_{j,J+1}+J^{\frac{1}{2}}\delta_{j,J-1}\}\{\delta_{j',J'+1}+\delta_{j',J'-1}\}.\end{aligned}\tag{63}$$

It is convenient to take the basis of our matrix in the following order:

$$\begin{array}{lccc} J= & 0 & 1 & 2\\ J'= & \underbrace{\cdots l-1,\,l,\,l+1,\,\cdots}_{n} & \underbrace{\cdots l-1,\,l,\,l+1,\,\cdots}_{n} & \underbrace{\cdots l-1,\,l,\,l+1,\,\cdots .}_{n}\end{array}$$

Then, it can easily be shown that a matrix

$$\mathbf{S}=\mathbf{s}+\mathbf{s}+\mathbf{s}+\cdots,\tag{64}$$

where $\mathbf{s}$ is a transformation matrix which diagonalizes the energy matrix of periodic potential problem, can transform our matrix (63) into the following form

$$\mathbf{V}=\mathbf{v}_1+\mathbf{v}_2+\cdots+\mathbf{v}_n,\tag{65}$$

where

$$\mathbf{v}_l=\frac{\mu^2}{R^3}\cos\frac{2l\pi}{n}\left(\begin{array}{ccccccc} 0 & 2(1/3)^{\frac{1}{2}} & 0 & 0 & \cdots & & \\ & 0 & 2(2/9)^{\frac{1}{2}} & 0 & \cdots & & \\ & & 0 & \cdots & \cdots & & \\ & & & \cdots & \cdots & & \\ & & & \cdots & \cdots & & \\ \text{symmetric} & & & & 0 & 2\{(J+1)/(6J+3)\}^{\frac{1}{2}} & \cdots\\ & & & & & 0 & \cdots\\ & & & & & & \cdots\end{array}\right),\tag{66}$$

In Eqs. (64) and (65), + means the direct sum.

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[35] W. Gordy, Revs. Modern Phys. **20**, 668 (1948).

TABLE II. Width parameter of rotational lines (linear molecules).

Molecule	μ (Debye)	J	$\Delta\nu_{\mathrm{obs}}$(Mc/mm Hg)	$\Delta\nu_{\mathrm{calc}}$
ICl	0.65	0→1	3.2[a]	2.9
		3→4	5.5[b]	0.8
HCN	2.88	0→1	25[c]	50
ClCN	2.5	1→2	25[d]	21.5
BrCN	2.94	2→3	21[d]	20
ICN	3.71	3→4	20[d]	24
OCS	0.72	1→2	6[d]	2

[a] R. T. Weidner, Phys. Rev. **72**, 1268 (1947).
[b] Townes, Merritt, and Wright, Phys. Rev. **73**, 1334 (1948).
[c] Smith, Gordy, Simmons, and Smith, Phys. Rev. **75**, 260 (1949).
[d] Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).

The eigenvalues of Eq. (66) may be approximated as follows. The eigenvector which corresponds to the lowest eigenvalue is

$$\left[1,1,\left(\frac{3}{2}\right)^{\frac{1}{2}},\left(\frac{2\cdot5}{3\cdot3}\right)^{\frac{1}{2}},\cdots\left(\frac{1\cdot3\cdot5\cdots3\cdot7\cdot11\cdots}{2\cdot4\cdot6\cdots1\cdot5\cdot9\cdots}\right)^{\frac{1}{2}},\right.$$
$$\left.\times\left(\frac{2\cdot4\cdot6\cdots5\cdot9\cdot13\cdots}{3\cdot5\cdot7\cdots3\cdot7\cdot11\cdots}\right)^{\frac{1}{2}},\cdots\right]. \quad (67)$$

Thus the lowest eigenvalue is

$$-\frac{4}{\sqrt{3}}\left(1+1+\frac{3}{2}+\frac{10}{9}+\ldots+\frac{1\cdot3\cdots3\cdot7\cdots}{2\cdot4\cdots1\cdot5\cdots}\right.$$
$$\left.+\frac{2\cdot4\cdots5\cdot9\cdots}{3\cdot5\cdots3\cdot7\cdots}+\ldots\right)^{-1}\nu\frac{\mu^2}{R^3}\cos\frac{2l\pi}{n}, \quad (68)$$

where ν is the order of the matrix (66). Since

$$\lim_{\nu\to\infty}\frac{1\cdot3\cdots3\cdot7\cdots}{2\cdot4\cdots1\cdot5\cdots}=\prod^{\infty}\frac{(n-1/2)(n-1/4)}{n(n-3/4)}$$
$$=\frac{\Gamma(1)\Gamma(7/4)}{\Gamma(3/2)\Gamma(5/4)}=1\cdot144\ldots,$$
$$\lim_{\nu\to\infty}\frac{2\cdot4\cdots5\cdot9\cdots}{3\cdot5\cdots3\cdot7\cdots}=\prod^{\infty}\frac{n(n+1/4)}{(n+1/2)(n-1/4)}$$
$$=\frac{\Gamma(1/2)\Gamma(5/4)}{\Gamma(1)\Gamma(3/4)}=1.311\ldots,$$

Eq. (68) is

$$-1.88(\mu^2/R^3)\cos(2l\pi/n) \quad (69)$$

at the limit $\nu\to\infty$.

The next eigenvalue can be approximately obtained if we neglect the first row and column of Eq. (66) and follow the same procedure as above. Successively taking the same procedure, we obtain the following series as an approximation to the eigenvalues

$$-1.88a,\ -1.79a,\ -1.77a,\ -1.76a,\ \cdots$$
$$a=(\mu^2/R^3)\cos(2l\pi/n). \quad (70)$$

In this approximation, the difference of the $(J-1)$th and Jth values is nearly $0.09/J^2$. In Eq. (70), the values are certainly too low except for the first,[36] so the first difference is too small. Moreover, we treated Eq. (66) as an infinite matrix, while actually it is of order about J^* if the rotational energy is of the same order of magnitude as the intermolecular perturbation at the rotational quantum number J^*. In the infinite matrix, the eigenvalue converges to $4a/6^{\frac{1}{2}}$, while in the finite matrix it tends to zero. From these two reasons, we may suppose that the difference of the $(J-1)$th and Jth eigenvalues is expressed by $0.2/J$.

The difference of the eigenvalues is small compared with the eigenvalue itself. If we can assume that all the eigenvalues are equal, the transformation by **T** in Eq. (13) can be omitted. In this case, our equation which determines the transition probability is

$$da_J/dt=\mu_{J,J-1}F\exp\left\{i\omega t-i\int^{t}(0.2\mu^2/(\hbar R^3J))\right.$$
$$\left.\times\cos(2l\pi/n)dt\right\}a_{J-1}. \quad (71)$$

Since the perturbation is proportional to R^{-3},

$$\Delta\nu=(\pi/2)\langle\{0.2\mu^2/(\hbar J)\}\cos(2l\pi/n)\rangle N$$
$$=\{0.2\mu^2/(\hbar J)\}N \quad (72)$$

by Eq. (27a). This formula is compared with experiment in Table II. Although general agreement is seen, a serious discrepancy occurs in the 3→4 line of ICl, the reason for which is not clear. It is possible that our theory, which neglects the energy difference between rotational states in comparison with the intermolecular interaction, may not be suitable to treat such molecules as HCN which have very small moments of inertia.

VIII. ROTATIONAL ABSORPTION LINE OF SYMMETRIC TOP MOLECULES

The matrix of the dipole interaction for this case is the one already given by Eq. (33). Since the eigenvalue of this matrix is very difficult to obtain, we shall approximate it by the diagonal element.

From the selection rule $\Delta M=0,\pm1$, we see that the orientation of the molecule scarcely changes in the optical transition. Thus, the difference of the intermolecular potential, which is required in the calculation of the width of absorption line $J-1$, $K\to J$, K, is

$$\Delta p=2(\mu^2/R^3)\{KK'MM'/[J'(J'+1)]\}$$
$$\times\{[J(J-1)]^{-1}-[J(J+1)]^{-1}\}\equiv\hbar\Delta\mu/R^3 \quad (73)$$

in our approximation. Since it is proportional to R^{-3}, the formula which gives the width is again Eq. (27a).

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[36] R. Courant and D. Hilbert, *Methoden der mathematischen Physik I* (Verlag. Julius Springer, Berlin, 1931), p. 28.

TABLE III. Width parameter of rotational lines (symmetric top molecules).

Molecule	μ (Debye)	I_a/I_c	J	$\Delta\nu_{\text{obs}}$ (Mc/mm Hg)	$\vert K\vert$	$\Delta\nu_{\text{calc}}$
CHF_3	1.59	0.55	1→2	18[a]	1→1 0→0	23 9
CH_3F	1.83	4.5	0→1	20[a]	0→0	23

[a] Gilliam, Edward, and Gordy, Phys. Rev. **75**, 1015 (1949).

TABLE IV. Width parameter of rotational lines (symmetric top molecules).

Molecule	I_a/I_c	J	$\Delta\nu_{\text{obs}}$ (Mc/mm Hg)	μ_{calc} (Debye)	μ_{calc}
PF_3	0.56	1→2 2→3	16[a]	1.6	1.5
CF_3Cl	1.7	2→3 3→4	50[b]	3.0	0.5
$CHBr_3$	0.15	0→1	0.8[c]	0.34	0.7

[a] Gilliam, Edward, and Gordy, Phys. Rev. **75**, 1015 (1949).
[b] D. K. Coles and R. H. Hughes, Phys. Rev. **76**, 858 (1949).
[c] Kojima, Tsukada, and Hagiwara, private communication.

The rotational energy of a symmetric top molecule is

$$E=aJ(J+1)+bK^2,\qquad a=\hbar^2/(2I_a),\quad b=\hbar^2\{(2I_c)^{-1}-(2I_a)^{-1}\},\tag{74}$$

where I_a and I_c are the principal moments of inertia of this molecule ($I_a=I_b$). In almost all molecules at room temperature, a and b are much smaller than kT. For this reason we can calculate the average of $|\Delta\mu|$ classically as

$$\begin{aligned}\langle|\Delta\mu|\rangle&=(\mu^2/\hbar)|K/(J^2-1)|\,|a/b|\,|(1+b/a)^{\frac{1}{2}}-1|\\&=(\mu^2/\hbar)|K/(J^2-1)|\\&\qquad\times\{I_c/|I_a-I_c|\}\,|(I_a/I_c)^{\frac{1}{2}}-1|.\end{aligned}\tag{75}$$

Thus the width parameter is

$$\begin{aligned}\Delta\nu=(\pi/2)(\mu^2/\hbar)|K/(J^2-1)|&\\\times\{I_c/|I_a-I_c|\}\,|(I_a/I_c)^{\frac{1}{2}}-1|N&\\\text{for } J-1, K\rightarrow J, K.&\end{aligned}\tag{76}$$

Another method is to use the root mean square of the eigenvalues. The corresponding eigenvalues of lower and upper states may not be so different for the usual collisions where J' is very large. In this case, the mean of the energy difference can be replaced by the difference of the mean. Using the root mean square and assuming the gaussian distribution, we have

$$\begin{aligned}\langle|\Delta\mu|\rangle=(8/3\pi)^{\frac{1}{2}}(\mu^2/\hbar)|K|&\\\times\{[J(J-1)]^{-\frac{1}{2}}-[J(J+1)]^{-\frac{1}{2}}\}&\\\times\{I_c/|I_a-I_c|\}\,|(I_a/I_c)^{\frac{1}{2}}-1|&\\\text{for } J-1, K\rightarrow J, K.&\end{aligned}\tag{77}$$

Although this result is formally different from Eq. (75), we can see that their numerical values are near.

Since the matrix **A** vanishes identically for $K=0$, we cannot use the above formula in this case. However we can use the preceding formula (72) because a symmetric top molecule with $K=0$ behaves like a linear molecule.

There are only a few experimental results with which we can compare our formula (76). In Table III, the line $J=1\rightarrow2$ of CHF_3 is composed of three lines corresponding to $K=1, 0, -1$, whose widths are separately shown in the table. If the splitting of these lines is much smaller than $\Delta\nu$, the width of the total line is about 15 Mc/mm Hg, which agrees with the experimental result.

There are some other results where the data are not so complete. In Table IV, the dipole moment is not known for all molecules, and J is not clearly cited in the original papers for two molecules. In the fifth column μ is estimated from the width by our formulas, and in the last column the same quantity is estimated from the other methods such as bond dipole moment or electronegativity scale. The very large value of $\Delta\nu$ for CF_3Cl may be due to the unresolved splitting of the components. Since Coles and Hughes observed the width at 0.1 mm Hg, the K splitting of about 2 Mc may be able to account for this large $\Delta\nu$.

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