Focusing of Carr-Purcell photon echoes, and collisional effects

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Since for echo formation the off-diagonal density matrix element σ_{ab} evolves from $\sigma_{ba} = \sigma^*_{ab}$ of the previous pulse, the eikonal $\varphi - \omega t$ reverses sign with each pulse. If the radius of curvature of the first $\pi/2$ pulse is R_1, the radius of curvature of the subsequent π pulses R_2, R_3, etc., the radius of curvature of the photon echo which follows the second pulse is $1/R_{E1} = 2/R_2 - 1/R_1$, the radius of curvature of the Carr-Purcell echo following the third pulse is given by $1/R_{E2} = 2/R_3 - 2/R_2 + 1/R_1$, and for subsequent Carr-Purcell echoes by $1/R_{E3} = 2/R_4 - 2/R_3 + 2/R_2 - 1/R_1$, etc. The influence of motion, adiabatic collisions, and velocity-changing collisions on the decay of echo amplitude is considered for curved wave fronts. Since the change in position from the constant-velocity position is important in the decay, a statistical theory for small displacement and its relationship to the forward scattering cross section is given. These results with r^{-3} and r^{-6} interactions between colliding molecules are compared with the experimental data for CH_3F and with an r^{-6} potential with the data for SF_6 and SiF_4.

I. INTRODUCTION

This paper considers the focusing of Carr-Purcell photon echoes and the effects of collision on the decay of the echo amplitude. An earlier paper[1] considered the focusing of the photon echo. The pulse sequence necessary to form a Carr-Purcell echo is shown in Fig. 1. The first pulse is usually a $\frac{1}{2}\pi$ pulse and at a time T later the second pulse is a π pulse. At time T after the second pulse an echo occurs and in the optical region is referred to as a photon echo.[2] The photon echo is analogous in the optical spectra region to the "spin echo" of Hahn[3] in the nuclear-magnetic-resonance region. Carr and Purcell[4] observed subsequent echoes in nuclear-magnetic-resonance studies and the echoes following the second, third, etc. π pulses are referred to as Carr-Purcell echoes. The optical analog of the Carr-Purcell echo was observed by Schmidt, Berman, and Brewer.[5] These experiments are often discussed in terms of the reversal of the time coordinate. At optical wavelengths the reversal of the eikonal $\varphi - \omega t$ which includes both the space- and time-phase components becomes important. It was this reversal which led to the suggestion of anomalous properties for the focusing of the photon echo.[1] Successive reversals lead to further anomalous properties for the Carr-Purcell photon echoes.

Since the decay of the amplitude of these echoes depends on adiabatic collisions, molecular motion across curved wave fronts, changes in molecular velocity, etc., some aspects of collisions are discussed. A small change in velocity between pulses has an important effect on the decay of the echo amplitude, and this effect was observed by Schmidt *et al.*[5] in their studies of echoes from CH_3F. They also recognized that the reversal aspect of Carr-Purcell echoes would limit this form of echo decay. Berman *et al.*[6] discuss the effect of molecular collisions on coherent optical transient phenomenon. I have discussed the importance of the forward scattering cross section for the decay of the photon-echo amplitude.[7] The transformation for the eikonal between the laboratory and molecular frames was incorrect in that paper and the order in which velocity-changing collisions occurred was not important. The error is corrected in this paper, and the order in which the collisions occur becomes important. A statistical theory to treat a sequence of weak collisions is developed. Again, measurements for large T provide a measurement of the total elastic cross section, and measurements for small T provide a measurement of the angular dependence of the forward scattering cross section. This method provides a direct relationship between the cross section and the decay of the echo amplitude for photon echoes and for Carr-Purcell echoes, and should be more useful than the Keilson-Storer velocity-jump model used by Schmidt *et al.*[5] and

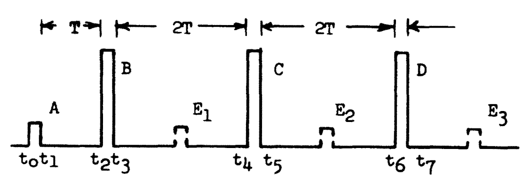

FIG. 1. Pulse sequence for the generation of a photon echo and the Carr-Purcell photon echoes. Pulse A starts at time t_0 and is a $\frac{1}{2}\pi$ pulse of duration $t_1 - t_0$. At time T later a π pulse E of duration $t_3 - t_2$ is applied. A photon echo E_1 is generated at time $t - t_3 = T$. The Carr-Purcell sequence begins with a π pulse C at time $t_4 - t_3 = 2T$ and the Carr-Purcell photon echo E_2 occurs at time $t - t_5 = T$. Subsequent π pulses create echoes E_3, E_4, etc.

Berman *et al.*[6] The experimental data for CH_3F are compared with the cross sections which are expected for an r^{-3} or a r^{-6} interaction potential between the colliding molecules. The large cross section[8] observed by this author and Nordstrom for SF_6 can be explained with the total elastic cross section of an r^{-6} interaction.

Although considerable care is used in setting up equations for the formation of echoes, some features must be either missing or overlooked in the analysis. The large, intensity-dependent cross section observed by Berman *et al.*[6] for CH_3F is not explained. The very large, pressure-independent cross section for echoes from SiF_4 which were observed by Nordstrom *et al.*[9] are not explained.

II. THEORY

A. General theory

The response of an atom or a molecule to a saturating pulse of radiation is described by the time-dependent Schrödinger equation,

$$i\hbar\,\partial\psi/\partial t=[H_0+V(t)]\psi\,, \qquad (1)$$

where the time-dependent perturbation $V(t) = -\vec{P}\cdot\vec{E}(\vec{r}_\alpha, t)$ for a molecule at position $\vec{r}_\alpha(t)$ connects the states $|J_a m_a)$ with $|J_b m_b)$. For a given angular frequency ω the interaction operator can be written as

$$V(t)=-\vec{P}\cdot(E\hat{u}e^{i[\varphi(r_\alpha)-\omega t]}+\text{c.c.})\,, \qquad (2)$$

where $\varphi(\vec{r})-\omega t$ is the phase or eikonal which describes a wave of geometrical optics. It is assumed that the wave normal of the laser radiation is primarily in the positive $\hat{z}$ direction. The operator[10]

$$A(t)=\exp\{i\tfrac{1}{2}\delta_0[\varphi(\vec{r}_\alpha(t))-\omega t]\} \qquad (3)$$

can be used to make the operator $V(t)$ independent of phase in the rotating-wave approximation, and with δ_0 defined as the operator

$$\delta_0=\sum_{m_a}|m_a)(m_a|-\sum_{m_b}|m_b)(m_b|, \qquad (4a)$$

the phase-independent interaction operator is

$$\begin{aligned}V_I&=A^+(t)V(t)A(t)\\&=-\hbar E\sum_{m_a m_b}|m_a)(m_b|(m_a|\vec{P}\cdot\hat{u}|m_b)+\text{H.c.}\,. \qquad (4b)\end{aligned}$$

δ_0 and $A(t)$ commute with the Hamiltonian

$$H_0=\sum_{m_a}|m_a)(m_a|E(m_a)+\sum_{m_b}|m_b)(m_b|E(m_b)\,. \qquad (5)$$

The unitary operator which describes the evolution of this system when the amplitude E changes from zero to E at time t_n is given by,

$$U(t,t_n)=A(t)e^{-i\xi(t-t_n)}A^+(t_n)\,, \qquad (6)$$

where the operator ξ is given by

$$\xi=\hbar^{-1}(H_0+V_I)+\tfrac{1}{2}\delta_0(\dot{\varphi}-\omega)\,, \qquad (7)$$

when $\dot{\varphi}$ is a constant. ξ is time independent and can be diagonalized in the representation $|\mu)$. In order to simplify the discussion, only the pseudo two-level problem of linear or of circular polarization is considered. The perturbation connects only the two states $|m_a)$ and $|m_b)$ where $m_a=m_b$ for linear polarization and $m_a=m_b\pm 1$ for right and left circular polarization. The matrix elements of $\exp(-i\xi\tau)$ are taken from Ref. 8, are summarized in an Appendix, and will appear as f or g in most of the subsequent equations. In the absence of a perturbation or $V=0$, the evolution of the system is described by

$$U(t,t')=e^{-iH_0(t-t')/\hbar}\,. \qquad (8)$$

The time dependence of the density matrix $\sigma_\alpha(t)$ for the αth molecule is given by

$$\sigma_\alpha(t)=U_\alpha(t,t_0)\sigma_\alpha(t_0)U_\alpha^+(t,t_0)\,, \qquad (9)$$

and the electric dipole moment of the radiating molecule is

$$\vec{P}_\alpha=\text{Tr}\vec{P}\sigma_\alpha(t)\,. \qquad (10)$$

Thus the quantity of primary interest after the interaction is turned on is the matrix element

$$\sigma_{ab}(t)=(m_a|\sigma_\alpha(t)|m_b)\,. \qquad (11)$$

Since only two states are connected by the perturbation which is used in this paper, the simplifying notation σ_{ab} is used. Whenever necessary these subscripts can be replaced by m_a, m_b and a sum taken.

The electric field generated at a distance r from this oscillating dipole is

$$\vec{E}_\alpha(\vec{r},t)=-\pi\left(\hat{k}\times\frac{(\hat{k}\times\vec{p}_\alpha)}{\epsilon_0\lambda^2 r}\right)e^{-i\omega(t-r/c)}+\text{c.c.}\,, \qquad (12)$$

where $\vec{p}_\alpha$ is the coefficient of $e^{-i\omega t}$ in Eq. (9). As a sum is taken over the spherical waves from a group of molecules, a new wave front $\varphi_E(\vec{r})$ approximately describes the sum. In the subsequent calculations the contribution of this group of molecules to the traveling wave

$$\exp\{i[\varphi_E(\vec{r})-\omega t]\} \qquad (13)$$

is proportional to the sum of the amplitudes over the molecular index α,

$$F=\sum_\alpha F_\alpha=\sum_\alpha\sigma_{ab}(t)\exp\{-i[\varphi_E(\vec{r}_\alpha(t))-\omega t]\}\,. \qquad (14)$$

The exact proportionality constant is not of interest in this paper, but can be obtained when necessary.[1]

In order to give the sequential development of the stimulated electric dipole moment which is caused by the pulses which are shown in Fig. 1 in its simplest form, $\sigma_{ab}(t)$ is given for optical nutation, free induction decay, photon echoes, and Carr-Purcell echoes. Before the start of the pulse at time t_0, the density matrix $\sigma(t_0)$ is regarded as composed of equally probable lower states $|m_b)$ or

$$\sigma(t_0) = (2J_b + 1)^{-1}|m_b)(m_b| . \tag{15}$$

If the upper state $|m_a)$ is populated, the number of molecules per cubic meter in the lower state $n(m_b)$ can be replaced[8] by $n(m_b) - n(m_a)$ in the expression for $n\sigma_{ab}$.

B. Optical nutation and free induction decay

If a pulse is turned on at $t = t_0 = 0$ as shown in Fig. 1, then the density matrix describing the effect is

$$\begin{aligned}\sigma_{ab}(t) &= (a|U_1(t, t_0)\sigma(t_0)U_1^\dagger(t, t_0)|b) \\ &= (a|e^{-i\xi_1(t-t_0)}|b)(b|e^{i\xi_1(t-t_0)}|b)e^{i(\varphi-\omega t)} \\ &= (-g_1 f_1)e^{i(\varphi-\omega t)} ,\end{aligned} \tag{16}$$

where $U_1(t, t_0)$ is given by Eq. (6) with $\xi = \xi_1$ or pulse amplitude E_1. Both f_1 and g_1 depend on the strength of the interaction and on the off resonance $\Delta_\alpha + \omega_{ab} - \omega + \dot\varphi_\alpha$, and detailed expressions are given in the Appendix. This stimulated electric dipole radiates, and a sum over molecular velocities which appears as different $\dot\varphi_\alpha$ or over inhomogeneous broadening which occurs as different ω_{ab} in Eq. (16) yields *optical nutation.*[5]

The pulse is turned off at $t = t_1$ and the evolution is described by the operator U_0 of Eq. (8). After time t_1 the density matrix is given by

$$\sigma_{ab}(t) = (-g_1 f_1)e^{i(\varphi_1-\omega_1 t_1)}e^{-i\omega_{ab}(t-t_1)} , \tag{17}$$

where $\tau_1 = t_1 - t_0$ in f_1 and g_1, $\varphi_1 = \varphi(\vec r_\alpha(t))$, and ω_1 is the pulse frequency. For a molecule at resonance, a $\frac{1}{2}\pi$ pulse yields a value of $f_1 = g_1 = 2^{-1/2}$. Substitution of $\sigma_{ab}(t)$ into Eq. (14) and the sum over the molecular index α yields the amplitude of the emitted radiation. This radiation is referred to as *free induction decay* and is dependent on those molecules interacting most strongly with the radiation.

C. Generation of echoes

The density matrix element $\sigma_{ab}(t)$ which describes the echo following the mth pulse in Fig. 1 follows in a direct manner from the density-matrix element $\sigma_{ba}(t_{2m-2})$ at time t_{2m-2} and is given by

$$\sigma_{ab}(t) = (a|R_{m-1}|b)(b|\sigma(t_{2m-2})|a)(a|R^\dagger_{m-1}|b) . \tag{18}$$

R_m is the operator which generates the mth echo and

$$R_{m-1} = U_0(t, t_{2m-1})U_m(t_{2m-1}, t_{2m-2}) , \tag{19}$$

where U_m is given by Eq. (6) and U_0 by Eq. (8) for the αth molecule. Direct evaluation yields $\sigma_{ab}(t)$ after the mth pulse of

$$\begin{aligned}\sigma_{ab}(t) = \sigma_{ba}(t_{2m-2})g_m^2 \exp\{i[\varphi_m(t_{2m-1}) + \varphi_m(t_{2m-2}) \\ -\omega_m(t_{2m-1} + t_{2m-2}) \\ -\omega_{ab}(t - t_{2m-1})]\} ,\end{aligned} \tag{20}$$

where g_m is given in the Appendix. For a π pulse for molecules at resonance, $g_m = 1$. Iteration of Eq. (20) with Eq. (17) for $\sigma_{ab}(t_2)$ yields all subsequent values of $\sigma_{ab}(t)$. The first echo, which is usually called the photon echo, occurs after the second pulse and follows from $\sigma_{ba}(t_2)$ and R_1. The second echo, which is the beginning of the Carr-Purcell echoes, depends on $\sigma_{ba}(t_4)$ and R_2; the third on $\sigma_{ba}(t_6)$ and R_3; and the mth echo on $\sigma_{ba}(t_{2m})$ and R_m. It is this dependence of $\sigma_{ab}(t)$ after the mth pulse on

$$\sigma_{ba}(t_{2m-2}) = \sigma^*_{ab}(t_{2m-2}) \tag{21}$$

which yields the reversal in sign of the phase in all terms prior to the time t_{2m-2}. It is this reversal which has led to the many fascinating explanations of nuclear spin echoes. In the optical region it gives rise to the additional effects of anomalous echo polarization which were studied by Heer and Nordstrom,[8] by Gordon *et al.*,[11] and by Abella *et al.*,[2] and to the suggestion of the focusing of photon echoes.[1]

For stationary molecules the terms $\dot\varphi_m$ are constant. For moving molecules each φ is replaced by

$$\varphi(\vec r_\alpha(t)) = \varphi(\vec r_\alpha(0)) + \int_0^t \dot\varphi_\alpha dt' , \tag{22}$$

and depends on the position at time $t_0 = 0$ and upon the Doppler shift $\dot\varphi$. In the absence of collisions $\dot\varphi$ is a constant, and the effect of velocity-changing collisions is introduced by writing φ as

$$\varphi(t) = \varphi + \dot\varphi_{0m}t + \int_0^t dt'[\dot\varphi(t') - \dot\varphi_{0m}] . \tag{23}$$

φ is for stationary molecule; $\dot\varphi_{0m}$ is the Doppler shift during the mth pulse and is used in g_m. The integral includes both the effects of collisions and of wave-front curvature. Collisions in the interval between pulses can cause a shift in phase as well as a shift in velocity, and this shift can be introduced for the interval $t'' - t'$ by the replacement

$$\omega_{ab}(t''-t') \to \omega_{ab}(t''-t') + \int_{t'}^{t''} \delta\omega_{ab}dt . \quad (24)$$

These collisional aspects will be discussed in greater detail in subsequent sections. In solids different molecules experience different local fields and ω_{ab} must be replaced by $\omega_{ab}(\vec{r})$. If Stark splitting occurs in gases, an inhomogeneity in the electric field will introduce another time-dependent term $\omega_{ab}(\vec{r}_\alpha(t))$.

A good approximation for $\dot{\varphi}_\alpha$ for the molecule with velocity $\vec{v}_\alpha$ is

$$\dot{\varphi}_\alpha \cong \vec{v}_\alpha \cdot \text{grad}\varphi_\alpha . \quad (25)$$

For plane waves $\varphi_\alpha = (\omega/c)\hat{k}\cdot\vec{r}_\alpha$ and $\dot{\varphi}_\alpha = (\omega/c)\hat{k}\cdot\vec{v}_\alpha$ is the usual Doppler shift. For spherical waves $\varphi = (\omega/c)R$, where R is the radius of curvature of the wave front and $\dot{\varphi} = (\omega/c)\dot{R} \cong (\omega/c)v_R$ is approximately given by Eq. (25). There is a quadratic term $v_\perp^2 t/R$ which depends on the transverse velocity component and on time. Even though experimental conditions favor $v_\perp \gg v_R$, the ratio $v_\perp^2 t/v_R R \ll 1$ and this time-dependent term can be ignored for the time intervals of interest.

1. Photon echo

Direct substitution of $\sigma_{ab}^*(t_2)$ from Eq. (17) into Eq. (20) yields $\sigma_{ab}(t)$ for the first echo or photon echo and the substitution of $\sigma_{ab}(t)$ into Eq. (14) yields the amplitude $F_{1\alpha}$ of

$$F_{1\alpha} = \{(-g_2^2 f_1^* g_1^*) e^{-i(\varphi_E - 2\varphi_2 + \varphi_1)} e^{-i\Delta_2(t-t_3-T)} \times G_2(t,t_3) G_2^*(t_2, t_2 - T) K_2\}_\alpha , \quad (26)$$

where $\Delta_2 = \omega_{ab} - \omega + \dot{\varphi}_{02}$ is used in g_2 and $\{\cdots\}_\alpha$ indicates all values are for a molecule described by $\vec{r}_\alpha$. Collisional effects are included in the $G_{2\alpha}$ terms. As a sum is taken over the molecular index α, the sum is zero unless the φ's differ by no more than a constant for the different values of $\vec{r}_\alpha(0)$ and the first condition for a photon echo is

$$\varphi_E - 2\varphi_2 + \varphi_1 = \text{const} . \quad (27)$$

In gases the molecular velocity or $\dot{\varphi}_\alpha$ is different for each molecule, and as the sum is taken over α, the amplitude F in Eq. (14) is large only when

$$t - t_3 = T . \quad (28)$$

For solids $\omega_{ab}(\vec{r}_\alpha)$ varies with position, and again this is the time condition for the occurrence of an echo. In the absence of collisions the G_2 are unity. When collisions occur, $G_2(t,t_3)$ cannot form a sequence with $G_2^*(t_2, t_2 - T)$ and these two quantities can be treated as statistically independent. The $G_{2\alpha}$ and subsequently the $G_{m\alpha}$ can be replaced by the single collision integral,

$$G = \left\langle \exp\left(-i\int_0^T dt'[\dot{\varphi}(t') - \dot{\varphi}(0) + \delta\omega_{ab}] \right) \right\rangle_c . \quad (29)$$

This quantity is similar to that used by Gyorffy, Borenstein, and Lamb[12] in their discussion of line broadening in gas lasers, and is discussed in the subsequent sections. For $G_2(t,t_3)$ the quantity with the square brackets in Eq. (29) is $[\dot{\varphi}_2(t) - \dot{\varphi}_{02} + \delta\omega_{ab}]$ and the limits of integration are from t_3 to t. It is assumed that the pulses are short and that collisional effects during the pulses can be ignored or $\dot{\varphi}_{02} = \dot{\varphi}_2(t_3) = \dot{\varphi}_2(t_2)$. The echo occurs at $t = t_3 + T$, and in forming the average the time origin can be shifted and the integral taken from 0 to T. By the same argument $G_2^*(t_2, t_2 - T)$ is integrated from 0 to T. K_2 is given by the integral

$$K_2 = \exp\left(-i\int_{t_2-T}^{t_3+T} dt' [\dot{\varphi}_{E1}(t') - \dot{\varphi}_2(t')] \right) , \quad (30)$$

and K is unity for plane waves in the z direction. For misaligned plane waves or curved wave fronts K is nonzero and its importance is discussed later. The primary decrease in photon-echo amplitude with interval T between pulses is given by

$$\ln(F_1/F_0) = 2\ln G , \quad (31)$$

and the factor of 2 is needed to include both $G_2(t_3+T, t_3)$ and $G_2^*(t_2, t_2 - T)$.

2. Carr-Purcell echoes

The second echo or the first Carr-Purcell echo follows from Eq. (20) with $\sigma_{ba}(t_4)$ and the echo amplitude in Eq. (14) has the form,

$$F_{2\alpha} = \{(-g_3^2 g_2^{*2} g_1 f_1) e^{-i(\varphi_E - 2\varphi_3 + 2\varphi_2 - \varphi_1)} \times e^{-i\Delta_3(t-t_5-T)} e^{i\Delta_2(T-t_2+t_1)} G_3(t,t_5) G_3^*(t_4, t_4 - T) \times G_2^*(t_3+T, t_3) G_2(t_2, t_2 - T) K_3 K_2^*\}_\alpha . \quad (32)$$

The conditions for the second echo are

$$\varphi_E - 2\varphi_3 + 2\varphi_2 - \varphi_1 = \text{const} \quad (33a)$$

and

$$t - t_5 = T . \quad (33b)$$

Since $T = t_2 - t_1$ the exponential with Δ_2 is unity and is retained to indicate the method which was used in arranging the terms. The G's cannot be placed in sequence and can be treated as statistically independent, and have the form of Eq. (29). Thus the decay of the second echo amplitude is given by

$$\ln(F_2/F_0) = 4\ln G . \quad (34)$$

The generalization to the mth echo is apparent from these two examples and the decay in echo amplitude is primarily due to

$$\ln(F_m/F_0) = 2m \ln G \,, \tag{35a}$$

and the decay in echo intensity by

$$\ln(I_m/I_0) = 4m \ln G \,. \tag{35b}$$

The decay in the logarithm of the echo amplitude decreases linearly in the echo number and depends through $\ln G$ on the interval T between pulses. This dependence was recognized as a useful experimental tool in the first papers on nuclear-magnetic-resonance echoes[4] or spin echoes.

D. Focusing of photon and of Carr-Purcell echoes

Focusing of photon echoes follows from Eq. (27) as one of the conditions for echo formation. Absolute phase is not important as long as it is the same for all molecules, and the gradient of Eq. (27) yields a relationship between wave normals of

$$\hat{n}_E = 2\hat{n}_2 - \hat{n}_1 \,, \tag{36}$$

where $\hat{n} = (c/\omega)\,\mathrm{grad}\varphi$. This equation must hold at every $\vec{r}_\alpha$ for the occurrence of large-amplitude echoes. For plane waves $\varphi_1 = \hat{k}_1 \cdot \vec{r}_\alpha$ for the first pulse, etc., and the echo direction follows from $\hat{k}_E = 2\hat{k}_2 - \hat{k}_1$. When $\hat{k}_2$ makes a small angle θ with $\hat{k}_1$, the echo direction $\hat{k}_E$ makes an angle 2θ with $\hat{k}_1$ and this angular dependence was observed by Abella *et al.*[2]

For spherical wave fronts $\varphi = \pm(\omega/c)R$ with the positive sign for diverging waves and the negative sign for converging waves and $\hat{n} = \pm\hat{R}$ can occur in Eq. (36). A simple geometrical construction with an off-axis point can be used to show that the radii of curvature of the wave fronts are related by

$$1/R_E = 2/R_2 - 1/R_1 \,, \tag{37}$$

where $R > 0$ for a diverging wave front and $R < 0$ for a converging wave front. If all wave fronts diverge for spherical waves, $\hat{R}_E = 2\hat{R}_2 - \hat{R}_1$ and the scalar product with a transverse unit vector yields $\sin\theta_E = 2\sin\theta_2 - \sin\theta_1$. For a selected point $R_1 \sin\theta_1 = R_2 \sin\theta_2 = R_E \sin\theta_E$ and these relationships for θ can be combined to yield Eq. (37). If both converging and diverging waves occur, this simple method with some care yields Eq. (37). This method is somewhat simpler than that used in an earlier paper,[1] but it does not include diffraction effects. The use of the eikonal approximation implies the usual limitations which occur in geometrical optics. Thus Eq. (36) for the wave normals is correct for small θ and terms of order θ^2 are neglected. Furthermore, a thin sample is required and this is apparent as the virtual source location R_E is determined for various positions in the sample.

Equation (33a) is one of the conditions for the formation of the second echo. The gradient of this equation yields a relationship between the wave normals of the first Carr-Purcell echo of

$$\hat{n}_E = 2\hat{n}_3 - 2\hat{n}_2 + \hat{n}_1 \tag{38a}$$

for every $\vec{r}_\alpha$. The second Carr-Purcell echo requires

$$\hat{n}_E = 2\hat{n}_4 - 2\hat{n}_3 + 2\hat{n}_2 - \hat{n}_1 \,, \tag{38b}$$

and $\hat{n}_E$ for subsequent echoes follows in an apparent manner. For plane waves the normals are the directions of the plane waves. As a special example one may note that if the odd-numbered pulses are along $\hat{k}_0$ and the even-numbered pulses along $\hat{k}_e$ with angle θ between $\hat{k}_0$ and $\hat{k}_e$ as shown in Fig. 2, the echo angle is given as follows: for the first echo, $+2\theta$; second echo, -2θ; third echo, $+4\theta$; fourth echo, -4θ; etc. with respect to $\hat{k}_0$. The echo angle increases by 2θ on the odd-numbered echoes and changes sign for even-numbered echoes.

For spherical wave fronts the first Carr-Purcell echo has a radius of curvature R_E which is given by

$$1/R_E = 2/R_3 - 2/R_2 + 1/R_1 \,, \tag{39a}$$

and the second Carr-Purcell echo has a radius of curvature

$$1/R_E = 2/R_4 - 2/R_3 + 2/R_2 - 1/R_1 \,. \tag{39b}$$

These relationships follow from Eq. (38) for the wave normals and can be derived in a manner which is similar to that used in deriving Eq. (37) for photon echoes. The radii of curvature of subsequent echoes follows in an apparent manner from Eq. (39). If the first pulse has a positive radius of curvature R_1 and the subsequent pulses are plane waves as shown in Fig. 3, the first echo

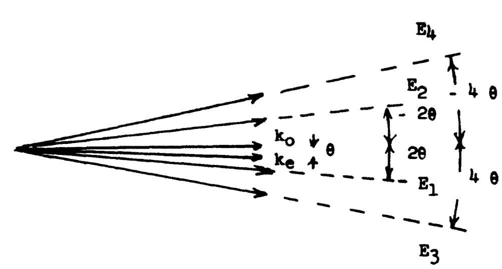

FIG. 2. The $\frac{1}{2}\pi$ pulse is along $\hat{k}_0$, the first π pulse is along $\hat{k}_e$, the second π pulse along $\hat{k}_0$, the third π along $\hat{k}_e$, etc. For an angle θ between $\hat{k}_0$ and $\hat{k}_e$, the first echo E_1 is in direction $\hat{k}_1$ at angle $+2\theta$ with $\hat{k}_0$, the second echo E_2 is in direction $\hat{k}_2$ at angle -2θ, the third echo is in direction $\hat{k}_3$ at angle $+4\theta$, etc.

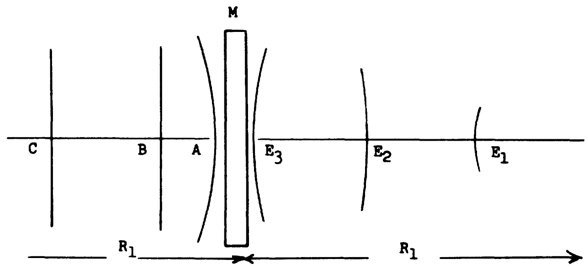

FIG. 3. The $\frac{1}{2}\pi$ pulse has a positive radius curvature R_1 and appears to diverge from a point at $-R_1$ to the left of the sample M. The following π pulses are plane waves. The radii of curvature of the Carr-Purcell photon echoes are given by Eq. (39). The first echo is converging toward a point $+R_1$ to the right of the sample M. The second echo is diverging and $-R_1$ is the virtual source. The third echo is converging toward $+R_1$. The fourth is diverging from $-R_1$; etc. for subsequent echoes.

is converging with a radius of curvature of $-R_1$, the second echo is diverging with $+R_1$, the third echo is converging with $-R_1$, etc. Again a thin sample is required.

1. Wave-front curvature

The effects of wave-front curvature are included in Eq. (30) for the K integrals. At any time t' Eqs. (36) and (38) imply

$$\dot{\varphi}_E - 2\dot{\varphi}_2 + \dot{\varphi}_1 = 0$$

for the first echo, $\dot{\varphi}_E - 2\dot{\varphi}_3 + 2\dot{\varphi}_2 - \dot{\varphi}_1 = 0$ for the second echo, etc. and these relationships can be used to write K_2 as given in Eq. (30) and K_m with $\dot{\varphi}_{E,\,m-1} - \dot{\varphi}_m$ as the integrand and t_{2m-2-T} to t_{2m-1+T} as the limits of integration. If the first pulse is in direction $\hat{k}_1$ and the second pulse in direction $\hat{k}_2$, then in Eq. (30) the integrand $\dot{\varphi}_E(t') - \dot{\varphi}_2(t') = (\omega/c)(\hat{k}_2 - \hat{k}_1)\cdot\vec{v}_\alpha \cong (\omega/c)\theta v_{\alpha y}$. In the absence of collisions a thermal average over v_y yields

$$K = \langle \exp[-i(4\pi\theta/\lambda)v_y T]\rangle = e^{-bT^2}, \qquad (40)$$

where $b = \pi^3(\theta\bar{v}/\lambda)^2$. Thus for a wavelength of $\lambda = 10^{-5}$ m and an average velocity $\bar{v}$ of 200 m/sec the angle θ can be no larger than 10^{-3} rad for $T \sim 10^{-5}$ sec and 10^{-2} rad for $T \sim 10^{-6}$ sec. Free molecular motion can place a restriction on the allowed angles between the wave normals of the pulses. Since curved wave fronts have angles between the wave normals from zero to $\theta_{\max}$, an average over these angles yields a somewhat smaller value of b and the condition is less restrictive. In a Carr-Purcell echo sequence this type term increases approximately as $\exp(-mbT^2)$ for the mth echo. It would seem possible to observe radii of curvature as small as $\frac{1}{2}$ m in the sample region. Collisions reduce the importance of this form of echo decay, but collisions which are sufficiently strong to change v_y by an appreciable amount will destroy the state and introduce a different form of echo decay.

III. COLLISIONS AND ECHO DECAY

It was shown in the previous section that a very important contribution to the decay of the echo amplitude by collisions is given by Eqs. (35) and (29). Equation (29) includes the effect of velocity-changing collisions and the effect of adiabatic collisions on $\delta\omega_{ab}$. Since a given collision changes both $\dot{\varphi}$ and $\delta\omega_{ab}$, it is not possible to arbitrarily consider the effects separately. In the subsequent sections the two effects are treated separately and then their magnitude and time dependence are used to suggest regions in which one effect dominates the other. Velocity-changing collisions are considered first, and with $\delta\omega_{ab} = 0$ Eq. (29) for G for plane waves in the z direction becomes

$$G_V = \left\langle \exp\left(-i\frac{\omega}{c}\int_0^T dt'\,[v_z(t') - v_z(0)]\right)\right\rangle_c . \qquad (41)$$

The integral is a measure of the displacement of the molecule relative to a constant-velocity displacement or $z(T) - z(0) - v_z(0)T$. For weak collisions this is a small quantity, and, in order to consider this average, a statistical theory for small displacements is developed.

A. Statistical theory for small displacements

Consider a distribution law for points on a line where $P(\eta_k = m) = p(m)$ is the probability for the random variable η_k to equal the integer m. The characteristic function[13] for this distribution law is given by

$$\psi(a) = \langle e^{ia\eta}\rangle = \sum_m p(m)e^{ima}. \qquad (42)$$

Let the sum of a group of mutually independent random variables with the same distribution law be denoted by X_N,

$$X_N = \sum_{k=1}^{N} \eta_k . \qquad (43a)$$

The characteristic function for this random variable X_N is given by

$$\psi_N(a) = \psi(a)^N , \qquad (43b)$$

and the probability of a value of M is given by the Fourier inversion formula

$$P(X_N = M) = \frac{1}{2\pi}\int_{-\pi}^{\pi} da\, e^{-iMa}\psi_N(a) . \qquad (43c)$$

For the particular case in which the probability of a particular value of N is given by the Poisson distribution, then the characteristic function for the compound distribution

$$P(X=M)=\sum_{N=0}^{\infty}(e^{-\bar{N}}\bar{N}^N/N!)P(X_N=M) \tag{44a}$$

follows by direct substitution of the integral representation for $P(X_N=M)$ and is

$$\Psi(a)=\exp\{\bar{N}[\psi(a)-1]\}. \tag{44b}$$

The Fourier inversion formula yields $P(X=M)$.

If events occur at the rate of α sec^{-1} so that $\bar{N}=\alpha T$ and $\alpha p(m)=\alpha_m$ is the average rate for a process of type m, the characteristic function becomes

$$\Psi(a)=\exp\left(T\sum_m \alpha_m(e^{ima}-1)\right). \tag{45}$$

This characteristic function is usually derived for only one α_m and then statistical independence is used to write $\Psi(a)$ as a product of the $\Psi_m(a)$. This type of expression is particularly useful in the study of the effect of binary collisions[13] on line shape when the order of the events is not of importance.

The order of events is of importance in the sum S_N which is defined as

$$S_N=\sum_{n=1}^{N}X_n=\sum_{n=1}^{N}\sum_{k=1}^{n}\eta_k$$

$$=\sum_{M=0}^{N}M\eta_{N+1-M}, \tag{46a}$$

where η_n occurs $N+1-n=M$ times in S_N. Again the η_n are mutually independent random variables and the characteristic function is a product of characteristic functions

$$\langle e^{iaS_N}\rangle=\prod_{M=0}^{N}\psi(Ma), \tag{46b}$$

where

$$\psi(Ma)=\sum_m p(m)\cos Mma. \tag{46c}$$

$p(m)$ is regarded as an even function of m and only the real part of $\exp(iMma)$ is needed in this paper. If the probability of a particular value of N is given by the Poisson distribution, then the characteristic function of the compound distribution is

$$\langle e^{iaS}\rangle=\sum_{N=0}^{\infty}\frac{e^{-\bar{N}}\bar{N}^N}{N!}\prod_{M=0}^{N}\psi(Ma). \tag{47}$$

The cumulant expansion is often of use and for small Ma

$$\ln\psi(Ma)\cong-\tfrac{1}{2}a^2M^2\langle m^2\rangle$$
$$+(1/4!)a^4M^4[\langle m^4\rangle-3\langle m^2\rangle^2]+\cdots. \tag{48a}$$

This quantity is readily summed over M to yield

$$\ln\langle e^{iaS_N}\rangle\cong-\tfrac{1}{12}a^2N(N+1)(2N+1)\langle m^2\rangle\cong-\tfrac{1}{6}N^3a^2\langle m^2\rangle. \tag{48b}$$

For large $\bar{N}$ the Poisson distribution is almost Gaussian with its maximum at $\bar{N}$, and $\langle\exp(iaS)\rangle$ is given by Eq. (48b) with N replaced by $\bar{N}$.

Now consider an example in which the interval of measurement T rather than N is known. The characteristic function of the compound distribution follows from Eq. (47) with $\bar{N}=\alpha T$ and

$$\langle e^{iaS}\rangle=\sum_{N=0}^{\infty}\frac{e^{-\alpha T}(\alpha T)^N}{N!}\prod_{M=1}^{N}\psi(Ma). \tag{49a}$$

$\psi=1$ for $N=0$. In principle, $P(S=S')$ can be found when $p(m)$ is given. It may be noted that as T increases $\psi(Ma)\to 0$ and only the *no-collision* or $N=0$ term is important. A good approximation for large T is

$$\langle e^{iaS}\rangle\cong e^{-\alpha T}\ \text{(large } T), \tag{49b}$$

and this characteristic function yields $P(S=0)=e^{-\alpha T}$ and $P(S=S')=0$ for $S'\neq 0$. If $p(m)$ is appreciable for small values of m, then there is a range of T for which ψ is positive and the approximation $\ln\psi\cong\psi-1$ can be used. If $\bar{N}=\alpha T\gg 1$ the Poisson distribution is almost Gaussian and has it maximum near $N=\bar{N}$, and these terms dominate the sum. A fair approximation is

$$\ln\langle e^{iaS}\rangle\cong\sum_{M=0}^{\bar{N}}[\psi(Ma)-1]$$
$$\cong\alpha T\int dm\,p(m)\left(\frac{\sin\alpha Tma}{\alpha Tma}-1\right), \tag{49c}$$

and this yields the linear term in T for large T and the T^3 and T^5 moments for small T. The T^5 moment is in error by terms of the order of $\langle m^2\rangle^2$.

If the η_k refer to a random walk in which the probability of a step of displacement m is given by $p(m)$, then X_N is the displacement for an N-step walk and S_N is the area under the curve when X_N is plotted as a function of N.

If the η_k are proportional to random changes in velocity which occur in time interval τ, then X_n is proportional to the velocity at time $n\tau$, and S_N is proportional to the displacement in time interval $N\tau$. It should be noted that X_n as a random variable yields $\langle S_N^2\rangle$ linear in N and is the diffusion condition. η_k as a random variable is useful for a sequence of small changes, but it will not yield diffusion.

B. Velocity-changing collisions

The decay in echo amplitude by velocity-changing collisions is determined by evaluating Eq. (41) for G_V by the statistical theory for small displacement. The change in the velocity component is due to binary collisions and the integral can be written as the sum

$$\int_0^T dt'\,[v(t')-v(0)]=\sum_{n=0}^{N}\Delta t_n[v(t_n)-v(0)]$$
$$=\sum_{n=0}^{N}\Delta t_n\sum_{k=1}^{n}\Delta v_k$$
$$=\sum_{n=0}^{N}\Delta v_n\left(T-\sum_{k=1}^{n}\Delta t_k\right), \tag{50}$$

where $\Delta v_k=v(t_k)-v(t_{k-1})$ is the change in the velocity component in the kth collision of an N-collision sequence. The change in velocity in a collision is related to the change in relative velocity by

$$\Delta v=v'_{Az}-v_{Az}=-(\mu/m_A)(V'_z-V_z), \tag{51}$$

where μ is the reduced mass. In an N-collision sequence $T\cong N\tau_N$ and τ_N is the average time between collisions. With $\Delta t_k=\tau_N+y_k$ the variable y_k can be treated as mutually independent random variables. Thus the total change in phase in a sequence of N binary collisions in interval T is given by

$$S_N=\kappa\sum_{n=1}^{N}\left((N+1-n)\tau_N-\sum_{k=1}^{n}y_k\right)\eta_n$$
$$\cong\kappa\,\tau_N\sum_{M=0}^{N}M\eta_{N+1-M}, \tag{52}$$

where

$$\kappa\eta_n=-(\omega/c)(\mu/m_A)(V'_z-V_z)$$

and $\kappa=(\omega/c)(\mu/m_A)$. The Δv_n or η_n can be treated as mutually independent random variables, and in forming the characteristic function $\langle\exp(iaS_N)\rangle$ a product over n can be used. A further average over y_k is needed. A good approximation is obtained with the assumption that $y_k=0$. Only the average number of collisions $\bar{N}=\alpha T$ which occur in interval T is known in the determination of G_V, and since G_V follows from Eq. (49) for $\langle\exp(iaS)\rangle$, only the binary-collision characteristic function is needed.

Since η_n depends on the change in relative velocity from V_z to V'_z in a binary collision, the characteristic function[7] follows from the probability of a change in velocity

$$\sum_m p(m)\to\alpha^{-1}n\int P(V^2)\,d\vec{V}\int V\sigma(V,\theta)\,d\Omega, \tag{53a}$$

and the substitution

$$\cos ma\to\cos\kappa\,\tau(V'_z-V_z)a. \tag{53b}$$

$\sigma(V,\theta)$ is the differential cross section for the change in relative velocity V by angle θ, and $P(V^2)$ is the Maxwell-Boltzmann distribution for velocities. $\langle\cdots\rangle_c$ is used to denote this collision average. The characteristic function

$$\psi(a)=n\alpha^{-1}\langle V\sigma(V,\theta)\cos\kappa\,\tau(V'_z-V_z)a\rangle_c \tag{54a}$$

can be used to find the probability of the subsequent change $\kappa\,\tau(V'_z-V_z)$ which is induced by a binary collision. It is convenient to transform to angular coordinates $d\vec{V}=2\pi\sin\beta\,d\beta\,V^2dV$, $d\Omega=\sin\theta\,d\gamma\,d\theta$, $(V'_z-V_z)=V[-\sin\beta\sin\theta\cos\gamma+(\cos\theta-1)\cos\beta]$, and average over[7] the random variable γ and β. After this average and for small θ,

$$\psi(a)\cong n\alpha^{-1}\left\langle V\sigma(V,\theta)\frac{\sin\kappa\,\tau V\theta a}{\kappa\tau V\theta a}\right\rangle_c. \tag{54b}$$

The small-angle change in a binary collision is correctly described by this characteristic function. The relative occurrence of collisions depends in greater detail on the velocities $\vec{v}_A$ and $\vec{v}_B$ of the colliding molecules, and this effect can be neglected for small-θ collisions.

The probability that the exponent in Eq. (41) for G_V has a value S follows from Eq. (49a) for $\langle\exp(iaS)\rangle$ with τ in Eq. (53) replaced by $\tau_N=T/N$. This probability can be used to find G_V, and this procedure is the same as the substitution $a=1$ in the expression for $\langle\exp(iaS)\rangle$. With these substitutions a fair approximation for G_V is developed by the procedure used for Eq. (49c), and echo decay by velocity-changing collisions is

$$\ln G_V\cong n\int_0^T dx\left\langle V\sigma(V,\theta)\left(\frac{\sin\kappa V\theta x}{\kappa V\theta x}-1\right)\right\rangle_c \tag{55a}$$
$$\cong -nT\langle V\sigma(V,\theta)\rangle_c\ \ (\text{large } T) \tag{55b}$$
$$\cong -n[\langle a_3V^3\rangle\kappa^2T^3-\langle a_5V^5\rangle\kappa^4T^5+\cdots]\ \ (\text{small } T). \tag{55c}$$

As T becomes large the integral over x of the sine term is limited in magnitude to $\pi/2\kappa V\theta$ and the remaining term grows linearly in T. This permits the determination of $\langle V\sigma(V,\theta)\rangle_c$ and indirectly the total elastic cross section. For T sufficiently small or $\kappa VT\theta < 1$ in the region in which $\sigma(V,\theta)$ is large, the moment expansion can be used to examine the coarse features of the differential cross section for small θ. a_3 and a_5 are the coefficients obtained when the sine transform over small θ is completed and only the average over the Maxwell-Boltzmann distribution of velocities remains. It would seem that the sine transform will contain terms similar to the expansion of $y^{-1}\sin y$ for small y.

Again it must be emphasized that $\sigma(V,\theta)$ must be large for small θ for Eq. (54) to be useful. Hard collisions which cause a large change in θ and which give rise to diffusion are not included. This is particularly evident when the cumulant expansion of Eq. (53a) is considered and it is observed that the second moment

$$\langle V\sigma(V,\theta)(V_z' - V_z)^2\rangle_c$$

is directly proportional to the B_d or $\Omega^{(1,1)}$ integral, which occurs in the theory of diffusion.[13,14] The $(V_z' - V_z)^2$ term reduces to the $V^2(1-\cos\theta)$ term in this diffusion integral, and at small θ there is negligible contribution to the integral. The importance of these small values of θ are enhanced by the $(\kappa T)^2$ term and become measurable. As θ increases $\sin\kappa V\theta x$ becomes a rapidly oscillating term and as values of θ are reached which are important for diffusion, these rapidly oscillating terms yield negligible contributions.

Equation (55) for $\ln G_V$ can be combined with Eq. (35a) to yield a decay in echo amplitude for the mth echo of

$$\ln(F_m/F_0) \cong -n[\langle V\sigma(V,\theta)\rangle_c]2mT \quad (\text{large } T) \qquad (56a)$$

$$\cong -n[\langle a_3V^3\rangle\kappa^2T^2 - \langle a_5V^5\rangle\kappa^4T^4 + \cdots]2mT \quad (\text{small } T). \qquad (56b)$$

Since T is the interval between pulses, $2mT$ is approximately the interval between the first pulse and the time of measurement of the mth echo. The echo amplitude decays exponentially with time $t = 2mT$, but the decay constant depends on the pulse interval for small T and on the total collision rate for large T.

The decay of the echo differs from the results in an earlier paper.[7] Owing to an error in the determination of the change in phase, the order in which the collisions occurred was not important, and the appropriate characteristic function was Eq. (44b) with Eq. (54b) for $\psi(a)$ and with $\tau = 2T$ in $\psi(a)$. Although the same sine transform is important for small T, the numerical constants are changed when the order of the sequence is important.

C. Adiabatic collisions

When the oscillating electric dipole moment of the molecule occurs between an upper state $|a)$ and a lower state $|b)$, the energy level spacing ω_{ab} which is a function of the distance between two colliding molecules can be important. One procedure[13] is to compute the interaction between the excited state $|a)$ and the lower state of another molecule and denote the interaction by C_U/r^n. A similar procedure with the lower state yields C_L/r^n, and the phase shift during the collision is given by

$$\hbar\dot{\zeta} = (C_U - C_L)/r^n = C'/r^n . \qquad (57)$$

A straight-line path is usually assumed, or $r^2 = b^2 + V^2t^2$, and the impact parameter b and the relative collision velocity become parameters in the theory. The decay in echo amplitude which is due to this type collision is given by Eq. (29) with $\dot{\varphi} = 0$. The decay in echo amplitude follows from the evaluation of

$$G_A = \left\langle \exp\left(i \int_0^T \delta\omega_{ab}\, dt\right)\right\rangle_c , \qquad (58)$$

where

$$\delta\omega_{ab} = \omega_{ab}(t) - \omega_{ab} = \sum_k \dot{\zeta}(t - t_k)$$

describes the collisional effects and the sequence in which the binary collisions occur is not important. A detailed treatment of this problem is given elsewhere.[13] It is equivalent to replacing m in Eq. (45) by the total change in phase $\zeta(\infty)$ in a binary collision and by using Eq. (53a) for $\alpha_m = \alpha p(m)$. $\zeta(\infty)$ for a binary collision with impact parameter b and relative velocity V is given by

$$\hbar\zeta(\infty) = C' \int_{-\infty}^{\infty} dt\,(b^2 + V^2t^2)^{-n/2}, \qquad (59)$$

and is the same as the phase shift 2δ in the eikonal scattering approximation. For an r^{-6} interaction $\zeta(\infty) = 3\pi C'/8\hbar b^5V$ and for an r^{-3} interaction $\zeta(\infty) = 2C'/\hbar b^2V$. Then

$$\ln G_A = n\langle V\sigma(e^{i\zeta(\infty)} - 1)\rangle_c T \qquad (60a)$$

$$= -n(\pi^2\hbar^{-1}|C'|)T \quad (\text{for } r^{-3}) \qquad (60b)$$

yields an echo decay linear in T. For an r^{-3} potential it is assumed that $\pm|C'|$ occurs with equal probability and only the cosine term occurs. $\pi^2C'/\hbar$ is proportional to one-half of the total cross section for the r^{-3} collision and is an indication that hard collisions, i.e. $\zeta(\infty) > 1$ are of primary importance.

For sufficiently short T the Carr-Purcell echo measurements almost eliminate the effect of velocity-changing collisions and then

$$\ln(F_m/F_0) = 2m \ln G_A . \tag{61}$$

Schmidt, Berman, and Brewer[5] emphasized this aspect in their discussion of their measurements on CH_3F and they also emphasized the similarity to nuclear-spin echo experiments.[4]

Even though velocity-changing collisions and adiabatic collisions occur at the same time and the change in direction is related to the change in phase, the effect of velocity-changing collisions also depends on the interval between collisions. Since this interval is not related to the change, it would seem that velocity-changing collisions and adiabatic collisions can be treated as statistically independent for short T, and

$$G = G_V G_A \quad (\text{small } T) \tag{62a}$$

for both the photon echo and the Carr-Purcell echoes. For large T for photon echoes the decay in echo amplitude is essentially the probability of no collision during the decay interval and

$$G = G_V \quad (\text{large } T). \tag{62b}$$

D. Collisions and the r^{-3} potential

If the rotation operator $R^{(1)}_{Mm}(\alpha, \beta, \gamma)$ defines the x, y, z axes relative to the space-fixed axes X, Y, Z in terms of the spherical basis vectors, the interaction operator for the interaction between two permanent dipoles is given by

$$U(r) = \frac{1}{4\pi\epsilon_0 r^3} \sum_{M,M'} \left((-)^M \delta_{MM'} - 3 \sum_{m,m'} R_{Mm} R_{-M'm'} r_m r_{m'} \right) \times \mu_{AM} \mu_{B-M'} . \tag{63}$$

μ_{AM} and $\mu_{B-M'}$ are the electric dipole operators for molecules A and B in the space-fixed frame. $\vec{r} = x\hat{x} + b\hat{z}$ is the intermolecular distance for motion in the x-z plane with impact parameter b. $\hat{r}$ is a unit vector with components $r_{\pm} = \mp 2^{-1/2} \sin u$ and $r_0 = \cos u$. For a symmetric vibrator-rotator this potential energy has a first-order diagonal component of

$$\frac{\mu_A \mu_B}{4\pi\epsilon_0 r^3} \frac{K_A K_B m_A m_B}{J_A(J_A+1)J_B(J_B+1)} f(\alpha, \beta, \gamma, u) , \tag{64}$$

where $f = 1 - 3(-\sin\beta \cos\gamma \sin u + \cos\beta \cos u)^2$ and μ_A and μ_B are the magnitudes of the vibrational electric dipole moments. Since $\hat{b}$ is not chosen as the axis of quantization, f does not have the usual $(1 - 3\cos^2 u)$ form.[15] For a straight-line collision path the eikonal phase 2δ or $\zeta(\infty)$ of Eq. (59) has the form

$$2\delta = \zeta(\infty) = 2C/\hbar b^2 V , \tag{65a}$$

where

$$C = \frac{\mu_A \mu_B}{4\pi\epsilon_0} \frac{K_A K_B m_A m_B}{J_A(J_A+1)J_B(J_B+1)} (\sin^2\beta \sin^2\gamma - \cos^2\beta) . \tag{65b}$$

For a particular collision the angles β and γ and the quantum numbers $v_A K_A J_A m_A$ and $v_B K_B J_B m_B$ are given. It is now assumed that only the molecule which interacts with the laser radiation has known quantum numbers and only $v_A K_A J_A m_A$ are given. As the collision average $\langle \cdots \rangle_c$ is formed, the probability of selecting $K_B J_B m_B$ as well as the angles β and γ for the plane of the motion must be included. For given $K_A J_A m_A$ the coefficient C is as often positive as negative, but in the collisional average only the absolute value of C is used. The average of $|\sin^2\beta \sin^2\gamma - \cos^2\beta|$ is approximately 0.5. The average over $|K_B||m_B|/J_B(J_B+1)$ yields $J_B(J_B+1)/(2J_B+1)^2$ and is of the order of $\frac{1}{4}$. C is further reduced by the $K_A m_A/J_A(J_A+1)$ term.

If the molecule interacting with the laser radiation has an upper molecular state A^* connected by the radiation to the lower state A, then the interaction of this upper molecular state with molecule B and the lower molecular state with the same molecule B differs by $C' = C_U - C_L$ or

$$C' = \left(\frac{\mu_{A^*} J_A(J_A+1)}{\mu_A J_{A^*}(J_{A^*}+1)} - 1 \right) C , \tag{66}$$

where C is given by Eq. (56b). $K_{A^*} = K_A$ is used and for linear polarization $m_{A^*} = m_A$.

Schmidt, Berman, and Brewer[5] have measured the amplitude of decay of the photon echo and of the Carr-Purcell echo in CH_3F as a function of pulse interval T. Their data have a large, intensity-dependent decay term, but after this term is removed their experimental data would seem to fit the equations

$$\ln(F_1/F_0) = -n(5.1 \times 10^{-15})\, 2T \quad (\text{large } T) \tag{67a}$$

$$= -n(2.8 \times 10^{-15} + 6.1 \times 10^{-5} T^2 + \cdots)\, 2T \quad (\text{small } T). \tag{67b}$$

For sufficiently small T, the Carr-Purcell echo amplitude decayed as

$$\ln(F_m/F_0) = -n(2.8 \times 10^{-15})\, 2m T . \tag{68}$$

The decay of the echo amplitude for large T can be compared with Eqs. (62b) and (56a). The results from an earlier paper[7] for the total cross section for a C/r^3 potential gave $\sigma(V) = 2\pi^2 C/\hbar V$ and

$$\langle V\sigma(V,\theta)\rangle_c = 2\pi^2 C/\hbar = 5.1\times10^{-15} \quad (\mathrm{m^3/sec}).$$

This yields a value of $C = 2.7\times10^{-50}$. It was noted in the discussion of Eq. (65b) for C that an average over trajectory angles, K_B, and m_B yielded a factor of the order $\frac{1}{8}$, and

$$\langle C\rangle = \frac{1}{8}\frac{\mu_E^2}{4\pi\epsilon_0}\frac{K_A m_A}{J_A(J_A+1)}\,.$$

With $\langle C\rangle = \frac{1}{16}(\mu_E^2/4\pi\epsilon_0)$, the dipole moment $\mu_E = 6.9\times10^{-30}$ C m and can be compared with the experimental value[16] of 6.1×10^{-30} C m. This is only approximate agreement. The $K_A = 3$, $J_A = 4$, $K_{A^*} = 3$, $J_{A^*} = 5$ transition was used, and m_A was not given. $K_A/J_A = 3/5$ and for the stimulated molecule these states occur with equal probability. A factor of $\frac{1}{2}$ was introduced to estimate the effect of $K_A m_A/J_A(J_A+1)$. Equation (65b) is only approximate, and there could be appreciable contribution from the second-order perturbation terms.

For small T the coefficient of the T^3 term can be compared with the coefficient of the T^3 term in Eq. (56b),

$$\langle a_3 V^3\rangle \kappa^2 = 6.1\times10^{-5}$$

The cross section $\sigma(V,\theta)$ for a r^{-3} potential is not available, but it is known to diverge logarithmically[17] for small θ and to have a total cross section of $2\pi^2 C/\hbar V = (\pi b_0)^2$. A cross section which may have some features of this cross section for small θ is a constant cross section for small θ and with $\hbar k = \mu V$,

$$\sigma(V,\theta) = (\pi/\alpha^2)k^2 b_0^4 \quad (0 < kb_0\theta < \alpha) \tag{69}$$

$$= 0 \qquad (kb_0\theta > \alpha)\,.$$

Then $\langle a_3V^3\rangle\kappa^2 = (\pi^2/36)(\alpha\hbar\kappa/\mu)^2 V$ where $\hbar\kappa/\mu = h/m_A\lambda$. For CH_3F and $\lambda = 9.6\times10^{-6}$ m laser radiation and $\overline{V} = 600$ m/sec, this coefficient is $2.3\times10^{-4}\alpha^2$. Comparison with the experimental value 6.1×10^{-5} yields good agreement with $\alpha = 0.5$. This simple cross section corresponds to an angular change in the relative velocity of $\theta < (2kb_0)^{-1}$. The angular change in a collision with the average relative velocity $\overline{V}$ is $\Delta V = \overline{V\theta}$ or

$$\Delta V = \hbar/2\mu\overline{b}_0 = 1.9 \text{ m/sec}\,.$$

The concept of a "velocity jump" has been introduced for the discussion of velocity-changing collisions. Berman, Levy, and Brewer[6] suggest a value of 0.85 for this "velocity jump", which can be compared with one-half of the value of the change in relative velocity. They use a Keilson and Storer collision kernel in their discussion of small velocity changes. It would seem that the more direct relationship to the scattering cross section $\sigma(V,\theta)$ which is given in this paper should provide a better model. Then as experimental measurements become better, it may be possible to measure the higher moments $\langle a_5V^5\rangle\kappa^4T^4$, etc. and yield a more direct measurement of the scattering cross section in the forward direction.

The average value of the adiabatic collision constant C' is related to the constant C by Eq. (66) and with $J_A = 4$ and $J_{A^*} = 5$, $C' = \frac{1}{3}C$. With the previous value of C,

$$\pi^2 C'/\hbar = 0.9\times10^{-15}$$

and with Eq. (60b) the expected decay rate by adiabatic collisions can be obtained. This term and the inelastic collision rate contribute to the decay rate of Carr-Purcell echoes of 2.8×10^{-15} which is given by Eq. (68).

It may be noted that the adiabatic and inelastic collision contribution to the relaxation rate is approximately one-half of the total elastic cross section. In an elementary model this is equivalent to the contribution of the elastic encounters in which the phase shift $2\delta_l > 1$ or the impact parameter $b < b_0$. This implies that encounters with $b < b_0$ cause a transition out of the $v_A K_A J_A m_A$ state.

E. Collisions and the r^{-6} potential

There is always an attractive C/r^6 Van der Waals long-range interaction between molecules. The phase shift $2\delta_l$ or $\zeta(\infty)$ for a straight-line collision path follows from Eq. (59) and

$$2\delta_l = \zeta(\infty) = 3\pi C/8\hbar V b^5 = (b_0/b)^5\,, \tag{70}$$

where $l\hbar = \mu V b$ and $\hbar k = \mu V$ is used. The impact parameter $b = b_0$ for $\zeta(\infty) = 1$, and with this notation the total cross section is

$$\sigma(V) = 2.4\pi b_0^2\,, \tag{71}$$

where $2.4 = \pi/\Gamma(\frac{2}{5})\sin\frac{1}{5}\pi$. The angular dependence of the cross section for small angles is difficult to obtain, but its approximate form follows from

$$f(k,\theta) \cong ik\int_0^\infty b\,db\,J_0(kb\theta)\left(1 - e^{i(b_0/b)^5}\right). \tag{72}$$

The amplitude $f(k,0)$ is a known integral and is related to the total cross section by $\sigma(V) = (4\pi/k)\,\mathrm{Im}f(k,0)$. For small θ Mason[18] *et al.* suggest that this integral has the approximate form

$$f(k,0)\exp[-\sigma(V)k^2\theta^2/8\pi]\,.$$

Since

$$\sigma(V,0) = |f(k,0)|^2 = k^2 b_0^4\left|\tfrac{1}{2}i^{-2/5}\Gamma(\tfrac{3}{5})\right|^2,$$

the choice of constant in the exponential is selected in this paper so that the $\sigma(V,\theta)$ integrates to almost the total cross section. Thus

$$\sigma(V,\theta)\cong 0.60k^2b_0^4e^{-(kb_0\theta/2)^2} \quad (73)$$

is selected as the approximate form for the small-angle scattering.

It is this sharp small-angle peak which will be observable in Eq. (55a). Direct integration over $2\pi\theta\, d\theta$ of the sine term yields Dawson's integral. This is not a particularly useful form and the expansion which yields Eqs. (55b) and (55c) is used. For large T, that is $\kappa VT/kb_0=(\hbar\kappa/\mu b_0)T>1$, the decay rate depends on $n\langle V\sigma(V,\theta)\rangle_c$ and

$$\gamma\cong n[2.4\pi(3\pi C/8\hbar\overline{V})^{2/5}\overline{V}] \,, \quad (74)$$

where $\langle V^{3/5}\rangle=\overline{V}^{3/5}$ is used. The data of Hamann[19] *et al.* which were obtained from the study of the second virial coefficient can be used to obtain a value of $C=4400\times10^{-79}$ J m^3 for SF_6 and $C=2500\times10^{-79}$ J m^3 for SiF_4. For SF_6 this yields an approximate value of $\overline{b}_0=17.5\times10^{-10}$ m and a cross section of

$$\sigma(\overline{V})=2300\times10^{-20}\,\text{m}^2 .$$

This cross section yields a decay rate of

$$\gamma=2.3\times10^5\ P_{mT} ,$$

and can be compared with the rate of 2×10^5 P_{mT} which was observed by Heer and Nordstrom.[8] The pressure is in units of millitorr. For SiF_4 the impact parameter $\overline{b}_0=15.2\times10^{-10}$ m and the approximate cross section is $\sigma(\overline{V})=1750\times10^{-20}$ m^2. This cross section yields a decay rate of $\gamma=2.0\times10^5$ P_{mT}. The experimental value of the echo decay measured by Nordstrom[9] *et al.* is pressure independent in the pressure range from 1 to 10 mT and corresponds to a rate of $\gamma=3\times10^5$ for excitation with the $P(30)$ CO_2 laser line. A similar pressure-independent linewidth was found by Nella[20] with Lamb-dip measurements. This pressure-independent feature is not explained.

The second virial coefficient[21] for CH_3F suggests a value of $C=152\times10^{-79}$ and $\overline{b}_0=7.8\times10^{-10}$ m. This yields a cross section of 450×10^{-20} m^2 and an echo decay rate of 2.7×10^{-15} $n=0.9\times10^5$ P_{mT}. This value is somewhat smaller than the observed rate of 5.1×10^{-15}. CH_3F has both a r^{-3} and a r^{-6} interaction potential between molecules and in second virial coefficient calculations the contribution of the r^{-3} term is a small perturbation. This need not be true when the total cross section is important and the r^{-3} term could dominate the r^{-6} term.

For sufficiently small T Eq. (55c) is appropriate. The exponentail cross section yields a value of

$$\langle a_3V^3\rangle\,\kappa^2=1.7\ (\hbar\kappa/\mu)^2\,\overline{V}$$

for the coefficient of the T^3 term. At a wavelength of 10.6 μm, one has $(\hbar\kappa/\mu)=2.6\times10^{-4}$ for SF_6. This term becomes important when $(\hbar\kappa/\mu b_0)T=1.5\times10^5$ $T<1$ or at pulse intervals shorter than 0.6 μsec.

APPENDIX

The matrix elements of the operator $\exp(-i\xi\tau)$ are taken from Ref. 8 and the matrix elements connecting states $|m_a)$ and $|m_b)$ follow from

$$e^{-i\xi(m_b)\tau}=e^{-i\psi\tau}[\,|m_a)(m_a\,|\,f(m_b)-|m_a)(m_b\,|g(m_b) + |m_b)(m_a\,|g^*(m_b) + |m_b)(m_b\,|f^*(m_b)]\,, \quad (A1)$$

where

$$2q(m_b)=[\Delta^2(m_am_b)+4\,|v\,|^2(J_b\,1m_bM\,|J_am_a)^2]^{1/2}, \quad (A2)$$

$$f(m_b)=\cos q(m_b)\tau-i[\,\Delta(m_am_b)/2q(m_b)]\sin q(m_b)\tau\,, \quad (A3)$$

$$g(m_b)=i[v/q(m_b)]\,(J_b\,1m_bM\,|J_am_a)\sin q(m_b)\tau\,, \quad (A4)$$

$$\Delta(m_a,m_b)=\omega(m_am_b)-\omega\,, \quad (A5)$$

$$\psi(m_a,m_b)=\tfrac{1}{2}\hbar^{-1}[E(m_a)+E(m_b)]\,. \quad (A6)$$

The strength of the interaction $v=\hbar^{-1}E(J_a\,||P||\,J_b)(2J_a+1)^{-1/2}$.

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