Intensity Correlations in Raman Scattering*

ALEXANDER L. FETTER†‡

Department of Physics, University of California, Berkeley, California

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Correlated counting rates in Raman scattering are proposed as a means of studying optical phonons in crystals. This technique may be used to measure both the lifetime and spatial coherence of the vibrational states. Experimental counting times are estimated to be the order of 50 μsec for the case of a gas laser as a light source.

I. INTRODUCTION

CORRELATED counting rates have been a subject of discussion and interest since Hanbury Brown and Twiss[1] found positive correlations between two coherent light beams. Each beam in their experiment is detected separately, so that the effect is an intensity correlation, rather than the more usual amplitude correlation, typified by the Michelson interferometer. The experiment was first explained by essentially classical wave phenomena.[1,2] Recently, a quantum-mechanical theory of intensity correlations has been developed[3] and applied to beams of scattered particles,[4] which contain information about the correlations in the target. In most practical situations, the incident beam is too weak to permit measurement of scattered intensity correlations. The development of the laser, however, makes such experiments feasible, and consequently this paper contains a detailed calculation of the scattering of a light beam from a crystal. As a specific example, we consider Raman scattering, in which an incident photon excites a lattice vibration in one of the optical modes. The scattered photons are measured in two detectors, whose output is multiplied in a correlator, as in Fig. 1. A variable delay line may
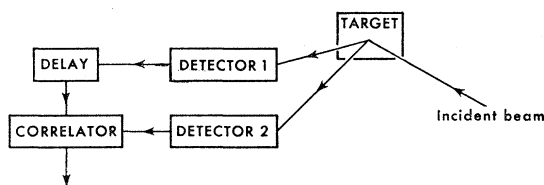

FIG. 1. Illustration of a general intensity-correlation experiment.

be inserted in the output of one of the detectors. Intensity correlations between the scattered photons can then be used to study both the lifetime and spatial coherence of the vibrational states.

A discussion of Raman scattering from crystals is given in Sec. II, together with a formulation of the incident and scattered beams. The amplitude correlation function and the cross section for Raman scattering are calculated in Sec. III. Our main interest, of course, is the intensity correlation function, which is computed in Sec. IV. The target correlations are contained in an unusual type of phonon correlation function, whose structure is studied in Sec. V with the aid of simple models. Detailed results are presented for diamond, which has a strong first-order Raman spectrum. Finally, Sec. VI contains a discussion of fluctuations in the correlated counting rates and an estimate of the time necessary for measurement with actual physical systems.

II. RAMAN SCATTERING BY CRYSTALS

The Raman effect in crystals is one in which an incident photon is scattered by the vibrations in the crystal lattice. The wave number of visible light ($\approx 10^5$ cm^{-1}) lies very close to the center of the first Brillouin zone, whose width is the order of 10^8 cm^{-1}. The wave number of the phonon is also approximately 10^5 cm^{-1}, so that momentum (as well as energy) is conserved with no additional reciprocal lattice vector. If a phonon is emitted, then the scattered photon has a lower frequency, and the transition is called a Stokes process. The opposite case, in which a phonon is absorbed, is called an anti-Stokes process. In thermal equilibrium, the Stokes process dominates when $\hbar\omega_0 \gg kT$, where ω_0 is the frequency of the phonon, k is Boltzmann's constant, and T is the equilibrium temperature of the lattice. For diamond, $\omega_0 \approx 2.51 \times 10^{14}$ rad/sec,[5] so that even at room temperature, the anti-Stokes process is negligible.

The theory of the Raman effect in crystals was first formulated by Born and Bradburn,[6] based on the polarizability tensor introduced by Placzek.[7] First-order

[1] R. Hanbury Brown and R. Q. Twiss, Nature **177**, 27 (1956); Proc. Roy. Soc. (London) **A242**, 300 (1957); **A243**, 291 (1958).

[2] E. M. Purcell, Nature **178**, 1449 (1956).

[3] R. J. Glauber, Phys. Rev. **130**, 2529 (1963); **131**, 2766 (1963); M. L. Goldberger, H. W. Lewis, and K. M. Watson, *ibid.* **132**, 2764 (1963); M. L. Goldberger and K. M. Watson, *ibid.* **134**, B919 (1964); R. J. Glauber, in *Quantum Optics and Electronics*, edited by C. DeWitt (Gordon and Breach Science Publishers, New York, 1965), p. 63.

[4] M. L. Goldberger and K. M. Watson, Phys. Rev. **137**, B1396 (1965).

[5] H. M. J. Smith, Phil. Trans. Roy. Soc. London **A241**, 105 (1948).

[6] M. Born and M. Bradburn, Proc. Roy. Soc. (London) **A188**, 161 (1947).

[7] G. Placzek, *Handbuch der Radiologie*, edited by E. Marx (Akademische Verlagsgesellschaft M. B. H., Leipzig, 1934), Vol. VI/2, p. 205.

transitions (emission or absorption of a single phonon) are forbidden if each lattice site is an inversion center. Thus diamond shows a first-order Raman effect,[5] while rock salt (NaCl) does not.[6] More recently, Loudon[8] has given a fully quantum-mechanical derivation of the Raman effect in crystals, which emphasizes the importance of the electrons in the scattering mechanism. The incident photon is absorbed, creating a virtual electron-hole pair. The pair emits or absorbs a phonon, and the crystal then returns to its initial state, emitting the scattered photon. The transition amplitude is calculated in third-order perturbation theory and contains $6 (\equiv 3!)$ terms, corresponding to the various possible time orderings of the three individual processes.

To simplify the calculations in this paper, the electrons will not be treated explicitly; instead, a model interaction Hamiltonian H_I is used, in which the photon emits or absorbs a phonon directly. The strength of the interaction is chosen to reproduce Loudon's calculated scattering cross section. The physical system considered here thus consists of photons and phonons contained in a volume V (the volume of the crystal), interacting through H_I. It is convenient to describe the system in the notation of second quantization. We introduce creation (annihilation) operators $a_\eta{}^\dagger(\mathbf{k}) (a_\eta(\mathbf{k}))$ that create (annihilate) one photon with wave vector $\mathbf{k}$ and polarization η.[9] These satisfy the usual Bose-Einstein commutation relations,

$$[a_\eta(\mathbf{k}), a_{\eta'}{}^\dagger(\mathbf{k}')] = \delta_{\eta\eta'}\delta_{\mathbf{kk}'}, \qquad (1)$$

where δ is the Kronecker delta. The permissible wave vectors form a discrete set because of the finite volume, and the index η takes on two values that specify the two independent states of polarization. The unperturbed photon Hamiltonian is

$$H_R = \sum_{\mathbf{k}\eta}(\hbar c k)[a_\eta{}^\dagger(\mathbf{k})a_\eta(\mathbf{k}) + \tfrac{1}{2}], \qquad (2)$$

where c is the speed of light. Equation (2) shows the equivalence between the radiation field and an assembly of uncoupled harmonic oscillators.

In a similar manner, the lattice vibrations are described by creation (annihilation) operators $b_\lambda{}^\dagger(\mathbf{q}) (b_\lambda(\mathbf{q}))$ that create (annihilate) one phonon with wave vector $\mathbf{q}$ in the branch λ. These operators also satisfy the Bose-Einstein commutation relations,

$$[b_\lambda(\mathbf{q}), b_{\lambda'}{}^\dagger(\mathbf{q}')] = \delta_{\lambda\lambda'}\delta_{\mathbf{qq}'}. \qquad (3)$$

For simplicity, we shall treat only lattices with two atoms per unit cell; in this case, the vibration spectrum has three acoustical branches and three optical

branches.[10] This work is restricted to optical modes, because the scattering from the acoustical modes (Brillouin scattering) is generally much weaker. The lattice Hamiltonian H_L is assumed to be the complete phonon Hamiltonian including both harmonic and anharmonic terms, but neglecting the effect of imperfections.

The total Hamiltonian for the photon-phonon system is

$$H = H_0 + H_I, \qquad (4)$$

where H_I is considered as a perturbation on the unperturbed Hamiltonian

$$H_0 = H_R + H_L. \qquad (5)$$

The form of H_I is taken to be

$$H_I = \sum_{\mathbf{ll'q}} \sum_{\eta\eta'\lambda} a_\eta(\mathbf{l})a_{\eta'}{}^\dagger(-\mathbf{l}')$$

$$\times [b_\lambda(\mathbf{q}) + b_\lambda{}^\dagger(-\mathbf{q})]v_{\eta\eta'\lambda}\delta_{\mathbf{l}+\mathbf{l}'+\mathbf{q},0}, \qquad (6)$$

in which a photon emits or absorbs a single phonon. In Eq. (6), the potential $v_{\eta\eta'\lambda}$ describes a transition from an initial state with a photon of polarization η to a final state with a photon of polarization η'; the associated phonon belongs to the branch λ. Strictly speaking, different potentials are associated with the emission and absorption of phonons, but the distinction is not important because only the dominant Stokes process is considered here. For calculations later in this work, it is important to introduce unit polarization vectors $\boldsymbol{\varepsilon}_{\mathbf{l}\eta}$ for the photons and $\mathbf{e}_{\mathbf{q}\lambda}$ for the phonons. The model potential may then be written in terms of the Raman tensor $R_{ii'}{}^j$

$$v_{\eta\eta'\lambda} = g(\omega_l\omega_{l'}\omega_{\mathbf{q}\lambda})^{-1/2}\sum_{ii'j} (\varepsilon_{\mathbf{l}\eta})_i(\varepsilon_{-\mathbf{l}'\eta'}{}^*)_{i'}(e_{\mathbf{q}\lambda})_j R_{ii'}{}^j, \qquad (7)$$

where the indices $ii'j$ refer to the Cartesian axes of the crystal.[11] Here ω_l is the frequency of a photon with wave number l, and $\omega_{\mathbf{q}\lambda}$ is the frequency of a phonon with wave vector $\mathbf{q}$ in the branch λ. The constant g is given by

$$g = (2\pi e^2/m^2 a\hbar)(\hbar/2MN)^{1/2}, \qquad (8)$$

where e, m are the charge and mass of the electron, a is the lattice spacing, M is the reduced mass of the two atoms in the unit cell and N is the total number of unit cells in the crystal. We shall frequently use the abbreviation

$$R_{\eta\eta'}{}^\lambda \equiv \sum_{ii'j} (\varepsilon_{\mathbf{l}\eta})_i(\varepsilon_{-\mathbf{l}'\eta'}{}^*)_{i'}(e_{\mathbf{q}\lambda})_j R_{ii'}{}^j, \qquad (9)$$

and the potential becomes

$$v_{\eta\eta'\lambda} = g(\omega_l\omega_{l'}\omega_{\mathbf{q}\lambda})^{-1/2}R_{\eta\eta'}{}^\lambda. \qquad (10)$$

[8] (a) R. Loudon, Proc. Roy. Soc. (London) A275, 218 (1963); (b) R. Loudon, Advan. Phys. 13, 423 (1964).

[9] The quantization of the electromagnetic field is treated in W. Heitler, The Quantum Theory of Radiation (Oxford University Press, Oxford, 1954), 3rd ed., Chap. I and II. A particularly clear discussion of the polarization of plane electromagnetic waves may be found in J. D. Jackson, Classical Electrodynamics (John Wiley & Sons, Inc., New York, 1962), pp. 205–207.

[10] A general discussion of phonons may be found in J. M. Ziman, Electrons and Phonons (Oxford University Press, Oxford, 1960), Chaps. I and III.

[11] An extensive table of the Raman tensor for various crystal symmetries is given in Ref. 8(b), pp. 440–447.

It is essential to use time-dependent perturbation theory since space and time correlations are the quantities of ultimate interest. For this purpose, the interaction representation[12] is most convenient, in which the time dependence of an operator O is governed by the unperturbed Hamiltonian H_0

$$O(t) = \exp(iH_0t/\hbar)O \exp(-iH_0t/\hbar) . \tag{11}$$

Thus the time-dependent photon and phonon operators are

$$a_\eta(\mathbf{k},t) = \exp(iH_Rt/\hbar)a_\eta(\mathbf{k}) \exp(-iH_Rt/\hbar)$$
$$= a_\eta(\mathbf{k}) \exp(-i\omega_k t) , \tag{12}$$

$$b_\lambda(\mathbf{q},t) = \exp(iH_Lt/\hbar)b_\lambda(\mathbf{q}) \exp(-iH_Lt/\hbar) , \tag{13}$$

where the commutation relations Eq. (1) have been used to derive the second line of Eq. (12). The standard treatment of phonon processes uses a somewhat different representation,[10] in which the time development of the phonon operators is governed solely by the harmonic part of the lattice Hamiltonian. In contrast, Eq. (13) contains the full lattice Hamiltonian and is particularly useful for the study of lifetime effects.

In the interaction representation, a state at time t is obtained from the same state at t_0 by the application of an operator $U(t,t_0)$,

$$|i\rangle = U(t,t_0)|t_0\rangle . \tag{14}$$

In particular, the final state $|f\rangle$ after the scattering has occurred is obtained from the initial state $|i\rangle$ before the scattering by Eq. (14),

$$|f\rangle = U(t,t_0)|i\rangle , \tag{15}$$

where $t(t_0)$ is long after (before) the scattering event. The operator U may be expanded in powers of H_I in the following manner:

$$U(t,t_0) = 1 - (i/\hbar) \int_{t_0}^{t} dt'H_I(t') + (i/\hbar)^2(2!)^{-1}$$
$$\times \int \int_{t_0}^{t} dt'dt''(H_I(t')H_I(t''))_+ + \cdots , \tag{16}$$

where the subscript $+$ means that the operators are positively time ordered, from right to left in ascending order.

The incident beam is assumed to be well collimated around a momentum $\hbar\mathbf{p}$ ($\mathbf{p}$ means wave vector, not momentum). The initial state $|i\rangle$ represents a given state of both the target and the beam. An ensemble average is taken over the target and beam states at the end of the calculation. For the target, this is merely a thermal average; for the beam, the ensemble depends on the details of the light source.

The formulation described in this section will now be used to calculate the correlation functions of the scattered beam.

III. AMPLITUDE CORRELATION FUNCTION

It is useful to introduce an operator $\varphi(\mathbf{y}t)$ that annihilates one photon at the space-time point $\mathbf{y}t$,

$$\varphi(\mathbf{y}t) = V^{-1/2} \sum_{\mathbf{k}\xi} \boldsymbol{\varepsilon}_{\mathbf{k}\xi}a_\xi(\mathbf{k},t)e^{i\mathbf{k}\cdot\mathbf{y}} , \tag{17}$$

where the origin of coordinates is in the crystal. The polarization of the annihilated photon lies along the direction of the vector $\boldsymbol{\varphi}$. By definition, the amplitude correlation function is[13]

$$\langle f| \varphi^\dagger(\mathbf{y}_2t_2)\varphi(\mathbf{y}_1t_1)|f\rangle . \tag{18}$$

As a preliminary step, it is simplest to compute the quantity

$$\varphi(1)|f\rangle = \varphi(1)U(t,t_0)|i\rangle , \tag{19}$$

where the abbreviation 1 has been introduced for $(\mathbf{y}_1t_1)$. The interaction Hamiltonian H_I that produces Raman scattering is weak, and the perturbation expansion Eq. (16) for U may be used. Since $\mathbf{y}_1$ lies out of the path of the incident beam, the first term of Eq. (16) does not contribute, and Eq. (19) becomes

$$\varphi(1)|f\rangle = -(i/\hbar)\varphi(1)\int_{t_0}^{t} dt'H_I(t')|i\rangle , \tag{20}$$

where higher order terms have been neglected. If only the Stokes process is included, Eq. (20) may be written explicitly as

$$\varphi(1)|f\rangle = -(i/\hbar V^{1/2}) \sum_{\mathbf{k}ll'} \sum_{\xi\eta\eta'\lambda} \int_{t_0}^{t} dt'e^{i(\mathbf{k}\cdot\mathbf{y}_1-\omega_k t_1)}$$
$$\times \boldsymbol{\varepsilon}_{\mathbf{k}\xi}a_\xi(\mathbf{k})a_\eta(\mathbf{l},t')a_{\eta'}^\dagger(-\mathbf{l}', t')$$
$$\times b_\lambda^\dagger(\mathbf{l}+\mathbf{l}', t')v_{\eta\eta'\lambda}|i\rangle , \tag{21}$$

where Eq. (12) has been used to replace $a_\xi(\mathbf{k},t)$ by $a_\xi(\mathbf{k})$.

The point $\mathbf{y}_1$ is many wavelengths from the crystal, and it is permissible to make an asymptotic evaluation in this limit.[4] The sum over $\mathbf{k}$ is replaced by an integral $(\sum_\mathbf{k} \rightarrow (2\pi)^{-3}V\int d^3k)$, and the angular integration is performed with the asymptotic formula

$$\int d\Omega_\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{y}}F(\hat{k}) = (2\pi/iky)e^{ iky}F(\hat{y}) , \tag{22}$$

where $\hat{k}$ and $\hat{y}$ are unit vectors. Equation (21) then vanishes unless $-\mathbf{l}' = k\hat{y}_1$ and $\eta' = \xi$, because the incident beam has no photons of momentum $\hbar k\hat{y}_1$. With this

[12] See, for example, S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Row, Peterson and Company, Evanston, Illinois, 1961), pp. 316–338.

[13] The correlation functions, Eqs. (18) and (42), when averaged over quantum states, are identical with those considered by Glauber in Ref. 3.

simplification, Eq. (21) reduces to

$$\varphi(1)|f\rangle = -\frac{V^{1/2}}{\hbar y(2\pi)^2}\sum_{\xi\lambda}\sum_{l\eta}\int_0^\infty k\,dk\int_{t_0}^t dt'$$

$$\times e^{ik(y_1-ct_1)}\varepsilon_{y_1\xi}a_\xi(k\hat{y}_1)a_\eta(\mathbf{l},t')$$

$$\times a_\xi^\dagger(k\hat{y}_1,t')b_\lambda^\dagger(\mathbf{l}-k\hat{y}_1,\,t')v_{\eta\xi\lambda}|i\rangle . \quad (23)$$

The frequency of the optical phonons for small **q** is essentially independent of **q**. Hence, in Eq. (23), the exponential dependence on k is given by $\exp[ik(y_1-ct_1+ct')]$. The integral over k may be evaluated approximately[4] by setting $k=k_1\equiv l-c^{-1}\omega_\lambda$ except in the exponent; this yields

$$\int_0^\infty k\,dk\,\exp[ik(y_1-ct_1+ct')]f(k)$$

$$\approx k_1 f(k_1)2\pi\delta(y_1-ct_1+ct') . \quad (24)$$

The delta function can then be used to perform the integration over t', with the result

$$\varphi(1)|f\rangle = -\frac{V^{1/2}}{2\pi\hbar y_1 c}\sum_{\xi\lambda}\sum_{l\eta}k_1\varepsilon_{y_1\xi}e^{il(y_1-ct_1)}$$

$$\times a_\xi(\mathbf{k}_1)a_\eta(\mathbf{l})a_\xi^\dagger(\mathbf{k}_1)b_\lambda^\dagger(\mathbf{l}-\mathbf{k}_1,\,\tau_1)v_{\eta\xi\lambda}|i\rangle , \quad (25)$$

where $\mathbf{k}_1\equiv k_1\hat{y}_1$, and τ_1 is a retarded time

$$\tau_1=t_1-y_1/c . \quad (26)$$

The calculation of the general amplitude correlation function is now straightforward. If the photon polarization is measured along the directions $\hat{n}_1$ and $\hat{n}_2$, Eq. (18) becomes

$$\langle f|\varphi^\dagger(2)\cdot\hat{n}_2\hat{n}_1\cdot\varphi(1)|f\rangle$$

$$=\frac{Vk_1k_2}{(2\pi\hbar c)^2 y_1 y_2}\sum_{\xi\lambda\xi'\lambda'}\sum_{l\eta l'\eta'}(\hat{n}_2\cdot\varepsilon_{y_2\xi'}{}^*)(\hat{n}_1\cdot\varepsilon_{y_1\xi})$$

$$\times\exp[il(y_1-ct_1)-il'(y_2-ct_2)]v_{\eta'\xi'\lambda'}{}^*v_{\eta\xi\lambda}$$

$$\times\langle i|b_{\lambda'}(\mathbf{l}'-\mathbf{k}_2,\,\tau_2)a_{\xi'}(\mathbf{k}_2)a_{\eta'}{}^\dagger(\mathbf{l}')a_{\xi'}{}^\dagger(\mathbf{k}_2)$$

$$\times a_\xi(\mathbf{k}_1)a_\eta(\mathbf{l})a_\xi^\dagger(\mathbf{k}_1)b_\lambda^\dagger(\mathbf{l}-\mathbf{k}_1,\,\tau_1)|i\rangle . \quad (27)$$

The initial states of the beam and target are independent, so that the matrix element separates into two factors. Furthermore, the initial state contains no photons of wave vector $\mathbf{k}_1$ and $\mathbf{k}_2$; with the use of the commutation relations, the amplitude correlation function simplifies to

$$\langle f|\varphi^\dagger(2)\cdot\hat{n}_2\hat{n}_1\cdot\varphi(1)|f\rangle$$

$$=\frac{Vk_1k_2}{(2\pi\hbar c)^2 y_1 y_2}\sum_{\xi\lambda\xi'\lambda'}\sum_{l\eta}\exp[il\{y_1-y_2-c(t_1-t_2)\}]$$

$$\times(\varepsilon_{y_2\xi'}{}^*\cdot\hat{n}_2)(\hat{n}_1\cdot\varepsilon_{y_1\xi})\langle i|a_\eta^\dagger(\mathbf{l})a_\eta(\mathbf{l})|i\rangle$$

$$\times\langle i|b_{\lambda'}(\mathbf{l}-\mathbf{k}_2,\,\tau_2)b_\lambda^\dagger(\mathbf{l}-\mathbf{k}_1,\,\tau_1)|i\rangle v_{\eta\xi'\lambda'}{}^*v_{\eta\xi\lambda} . \quad (28)$$
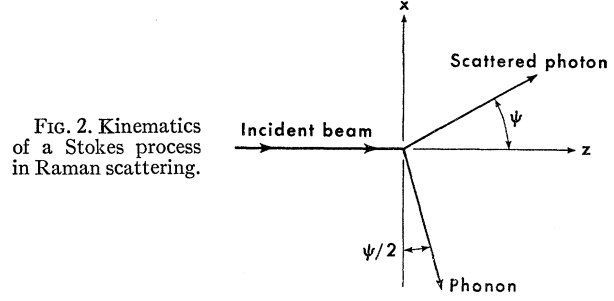

FIG. 2. Kinematics of a Stokes process in Raman scattering.

In the special case that $y_1t_1=y_2t_2$ and $\hat{n}_1=\hat{n}_2$, the amplitude correlation function is particularly interesting, for it then represents the density of scattered photons at y_1t_1, polarized along $\hat{n}_1$. If, in addition, we sum $\hat{n}_1$ over the three perpendicular coordinate directions, Eq. (28) measures the photon density, independent of polarization, and may be rewritten as

$$\langle f|\varphi^\dagger(1)\cdot\varphi(1)|f\rangle$$

$$=\frac{Vk_1^2}{(2\pi\hbar c y_1)^2}\sum_{\xi\lambda}\sum_{l\eta}|v_{\eta\xi\lambda}|^2\langle i|a_\eta^\dagger(\mathbf{l})a_\eta(\mathbf{l})|i\rangle$$

$$\times\langle i|b_\lambda(\mathbf{l}-\mathbf{k}_1,\,\tau_1)b_\lambda^\dagger(\mathbf{l}-\mathbf{k}_1,\,\tau_1)|i\rangle , \quad (29)$$

where λ' has been set equal to λ because the two phonon operators refer to a common time. The thermal average over the target states merely replaces the phonon matrix element by $\langle n_\lambda(\mathbf{l}-\mathbf{k}_1)+1\rangle$, where the number operator is defined by $n_\lambda(\mathbf{q})=b_\lambda{}^\dagger(\mathbf{q})b_\lambda(\mathbf{q})$ and $\langle\cdots\rangle$ indicates an ensemble average. If the beam is well collimated and has a well-defined frequency, as in a gas-laser beam, the sum over $\mathbf{l}\eta$ may be replaced by the single term $\mathbf{l}\eta=\mathbf{p}\zeta$, where $\mathbf{p}\zeta$ is the wave vector and polarization of the incident beam. In this limiting case, the density of scattered photons is

$$\langle f|\varphi^\dagger(1)\cdot\varphi(1)|f\rangle$$

$$=Vg^2(\omega_{k_1}/\omega_p)(2\pi\hbar c^2 y_1)^{-2}$$

$$\times\langle i|a_\zeta^\dagger(\mathbf{p})a_\zeta(\mathbf{p})|i\rangle$$

$$\times\sum_{\xi\lambda}\omega_\lambda^{-1}\langle n_\lambda+1\rangle|R_{\zeta\xi}{}^\lambda|^2 , \quad (30)$$

where Eq. (10) has been used to write v in terms of the Raman tensor.

The sum over polarizations must be calculated for a specific crystal symmetry. Loudon[11] gives a detailed treatment of the form of $R_{ii'}{}^j$ for the different point groups. In the case of diamond, $R_{ii'}{}^j=R$ if all three indices are different, and is zero otherwise. As a specific example, consider the incident beam along the z axis of the diamond crystal, with the photon scattered at an angle ψ_1 in the xz plane. This is shown in Fig. 2, where the approximation $\omega_\lambda\ll cp$, $k_1=p$ has been made. For small wave vectors, one phonon mode is longitudinal and two are transverse, all with a single degenerate frequency. If the incident photon is polarized at an angle

χ with respect to the xz plane, it is not difficult to show that

$$\sum_{\xi\lambda}\omega_\lambda^{-1}\langle n_\lambda+1\rangle|R_{\bar{\zeta}\xi}{}^\lambda|^2$$
$$=\omega_0^{-1}\langle n_0+1\rangle|R|^2\{1+\cos^2\chi\ \sin^2\psi_1\}\ ,\quad (31)$$

where the subscript 0 refers to the degenerate optical phonons.

In an actual experiment, Eq. (29) must be integrated over the sensitive volume of the finite detector of area Σ_1, width w_1, and efficiency γ_1. Furthermore, the response time of the detector must be taken into account through a response function $L_1(t_1)$. We shall follow Goldberger and Watson[4] and write the counting rate in the detector as

$$G_1=\int\ (1)\langle f|\ \boldsymbol{\varphi}^\dagger(1)\cdot\boldsymbol{\varphi}(1)|f\rangle\ ,\qquad (32)$$

where

$$\int\ (1)\cdots\equiv\int_{-\infty}^\infty dt_1 L_1(T_1-t_1)\int_1 d^3y_1\gamma(\mathbf{y}_1)\cdots.\quad (33)$$

For subsequent calculations, it is useful to introduce the Fourier transform $B_1(\omega)$ of the response function,

$$L_1(t)=(2\pi)^{-1}\int_{-\infty}^\infty\ d\omega B_1(\omega)e^{-i\omega t}.\qquad (34)$$

An ensemble average must be taken over the initial states, and the measured counting rate is

$$\langle G_1\rangle=\mathrm{Tr}[\rho_B\rho_T G_1]\ ,\qquad (35)$$

where $\rho_B(\rho_T)$ is the density matrix of the incident beam (target). Since the target is in thermal equilibrium, ρ_T is merely the canonical density matrix at a fixed temperature. The effect of the ensemble average is to replace $\langle i|a_{\bar{\zeta}}{}^\dagger(\mathbf{p})a_{\bar{\zeta}}(\mathbf{p})|i\rangle$ in Eq. (30) by

$$\langle a_{\bar{\zeta}}{}^\dagger(\mathbf{p})a_{\bar{\zeta}}(\mathbf{p})\rangle\equiv\mathrm{Tr}[\rho_B a_{\bar{\zeta}}{}^\dagger(\mathbf{p})a_{\bar{\zeta}}(\mathbf{p})]\ .\qquad (36)$$

If the detector is small, the variable y_1 may be replaced by the distance Y_1 from the crystal to the detector. With Eqs. (30) and (32)–(36), the mean counting rate is

$$\langle G_1\rangle=B_1(0)\frac{\Sigma_1}{Y_1^2}w_1\gamma_1\frac{Vg^2}{(2\pi\hbar c^2)^2}\frac{\omega_{k_1}}{\omega_p\omega_0}\langle a_{\bar{\zeta}}{}^\dagger(\mathbf{p})a_{\bar{\zeta}}(\mathbf{p})\rangle$$

$$\times\langle n_0+1\rangle|R|^2\{1+\cos^2\chi\ \sin^2\psi_1\}\ .\quad (37)$$

For most purposes, $B_1(0)$ may be set equal to one, which is valid for a low-pass filter.[4]

The incident flux may be calculated from the quantity $\langle i|\ \boldsymbol{\varphi}^\dagger(\mathbf{y}t)\cdot\boldsymbol{\varphi}(\mathbf{y}t)|i\rangle$; from Eq. (17), this is

$$\langle i|\ \boldsymbol{\varphi}^\dagger(\mathbf{y}t)\cdot\boldsymbol{\varphi}(\mathbf{y}t)|i\rangle=V^{-1}\langle i|a_{\bar{\zeta}}{}^\dagger(\mathbf{p})a_{\bar{\zeta}}(\mathbf{p})|i\rangle\ .\quad (38)$$

The average number of particles incident on a unit area per unit time is the flux F, where

$$F=cV^{-1}\langle a_{\bar{\zeta}}{}^\dagger(\mathbf{p})a_{\bar{\zeta}}(\mathbf{p})\rangle\ .\qquad (39)$$

It is also convenient to consider a calibrated detector, such that $\gamma_1=c/w_1$. The mean counting rate then becomes

$$\langle G_1\rangle=B_1(0)\frac{\Sigma_1}{Y_1^2}\left(\frac{Vg}{2\pi\hbar c^2}\right)^2\frac{\omega_{k_1}}{\omega_p\omega_0}F\langle n_0+1\rangle$$

$$\times|R|^2\{1+\cos^2\chi\ \sin^2\psi_1\}\ ,\quad (40)$$

which reproduces Loudon's result.[8] The differential cross section is

$$d\sigma/d\Omega=\langle G_1\rangle\{B_1(0)\Sigma_1 Y_1^{-2}F\}^{-1}$$

$$=\frac{e^4 V^2\omega_{k_1}\langle n_0+1\rangle|R|^2}{2\hbar^3 m^4 a^2 M N c^4\omega_p\omega_0}\{1+\cos^2\chi\ \sin^2\psi_1\}\ ,\quad (41)$$

where Eq. (8) has been used. The numerical value of $d\sigma/d\Omega$ is approximately $10^{-6}-10^{-7}$ cm^2/sr for a crystal volume of 1 cm^3.[8] It can be seen from Eq. (41) that the number of scattered photons is proportional to the volume of the crystal.

IV. INTENSITY CORRELATION FUNCTION

The intensity correlation function is defined as

$$\langle f|\hat{n}_2\cdot\boldsymbol{\varphi}^\dagger(2)\hat{n}_1\cdot\boldsymbol{\varphi}^\dagger(1)\hat{n}_1\cdot\boldsymbol{\varphi}(1)\hat{n}_2\cdot\boldsymbol{\varphi}(2)|f\rangle\ ,\quad (42)$$

where the photon polarizations at 1 and 2 are measured along the directions $\hat{n}_1$ and $\hat{n}_2$. A schematic experimental apparatus to measure Eq. (42) has been shown in Fig. 1. The calculation proceeds as in Sec. III, but is considerably longer. The operator U must now be expanded to second order, because two separate scattering events are involved. It is simplest to consider the quantity

$$\hat{n}_1\cdot\boldsymbol{\varphi}(1)\hat{n}_2\cdot\boldsymbol{\varphi}(2)|f\rangle$$

$$\approx\hat{n}_1\cdot\boldsymbol{\varphi}(1)\hat{n}_2\cdot\boldsymbol{\varphi}(2)(i/\hbar)^2(2!)^{-1}$$

$$\times\int\int_{t_0}^t dt'dt''(H_I(t')H_I(t''))_+|i\rangle\ ,\quad (43)$$

where Eq. (16) has been used. The evaluation of Eq. (43) is similar to Eqs. (20)–(26), and the result for a double Stokes process is

$$\hat{n}_1\cdot\boldsymbol{\varphi}(1)\hat{n}_2\cdot\boldsymbol{\varphi}(2)|f\rangle$$

$$=\frac{V}{(2\pi\hbar c)^2 y_1 y_2}\sum_{\xi\lambda\xi'\lambda'}\sum_{1\eta 1'\eta'}k_1 k_2\exp[il(y_1-ct_1)$$

$$+il'(y_2-ct_2)](\hat{n}_1\cdot\boldsymbol{\varepsilon}_{y_1\xi})(\hat{n}_2\cdot\boldsymbol{\varepsilon}_{y_2\xi'})$$

$$\times a_\xi(\mathbf{k}_1)a_{\xi'}(\mathbf{k}_2)[a_\eta(1)a_\xi{}^\dagger(\mathbf{k}_1)b_\lambda{}^\dagger(\mathbf{l}-\mathbf{k}_1,\tau_1)$$

$$\times a_{\eta'}(\mathbf{l}')a_{\xi'}{}^\dagger(\mathbf{k}_2)b_{\lambda'}{}^\dagger(\mathbf{l}'-\mathbf{k}_2,\tau_2)]_+|i\rangle$$

$$\times v_{\eta\xi\lambda}v_{\eta'\xi'\lambda'}\ .\quad (44)$$

The factor $(2!)^{-1}$ has been cancelled by the two ways of combining the annihilation operators in the factors

φ with the creation operators in the factors H_I. The time ordering of the photon operators in Eq. (44) is irrelevant, since the incident and scattered photons lie in different directions (and thus commute).

The intensity correlation function can be computed from Eq. (44) with no difficulty. The matrix element between initial states factors into one containing twelve photon operators and one containing four phonon operators. The photon matrix element may be simplified because the initial state has no photons with the wave vectors lying along $\hat{y}_1$ or $\hat{y}_2$. We shall sum independently over the three perpendicular directions of $\hat{n}_1$ and $\hat{n}_2$, so that the polarization of the scattered photons is not measured. The intensity correlation function then becomes

$$\langle f| \varphi^\dagger(2)\varphi^\dagger(1):\varphi(1)\varphi(2)|f\rangle$$

$$=\frac{V^2}{(2\pi\hbar c)^4(y_1y_2)^2}\sum_{\xi\xi'}\sum_{\lambda\mu\lambda'\mu'}\sum_{l\eta l'\eta'}k_1{}^2k_2{}^2$$

$$\times\langle i| a_{\eta'}{}^\dagger(l')a_\eta{}^\dagger(1)a_\eta(1)a_{\eta'}(l')|i\rangle$$

$$\times\{\langle i|[b_{\mu'}(l'-\mathbf{k}_2,\tau_2)b_\mu(l-\mathbf{k}_1,\tau_1)]_-$$

$$\times[b_\lambda{}^\dagger(l-\mathbf{k}_1,\tau_1)b_{\lambda'}{}^\dagger(l'-\mathbf{k}_2,\tau_2)]_+|i\rangle$$

$$\times v_{\eta'\xi'\mu'}{}^* v_{\eta\xi\mu}{}^* v_{\eta\xi\lambda} v_{\eta'\xi'\lambda'}$$

$$+\exp[i(l-l')\{y_1-y_2-c(t_1-t_2)\}]$$

$$\times\langle i|[b_{\mu'}(l-\mathbf{k}_2,\tau_2)b_\mu(l'-\mathbf{k}_1,\tau_1)]_-$$

$$\times[b_\lambda{}^\dagger(l-\mathbf{k}_1,\tau_1)b_{\lambda'}{}^\dagger(l'-\mathbf{k}_2,\tau_2)]_+|i\rangle$$

$$\times v_{\eta\xi'\mu'}{}^* v_{\eta'\xi\mu}{}^* v_{\eta\xi\lambda} v_{\eta'\xi'\lambda'}\} . \quad (45)$$

Here the double scalar product implied by : is taken between the pairs of operators at the same point, and the subscript $-$ means negative time ordering. The two terms are conventionally described as "direct" and "exchange" respectively. Equation (45) also contains additional terms proportional to $\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\xi\xi'}$, which contribute only when the two detectors in Fig. 1 are replaced by a single detector. These terms lead to a negligible correction of order $V^2\Sigma^{-1}(pV^{1/3})^{-2}\ll1$, after Eq. (45) is integrated over the finite size of the detector.

The narrow width of the laser beam permits replacement of the sums over $l\eta$ and $l'\eta'$ by the single term $p\zeta$. For a typical beam frequency width of $\Delta\omega_B\approx10^7$ rad/sec, this approximation requires that $|y_1-y_2-c(t_1-t_2)|\ll c/\Delta\omega_B\approx3\times10^3$ cm. The remainder of this paper is therefore limited to spatial separations $|y_1-y_2|\ll3\times10^3$ cm and temporal separations $|t_1-t_2|\ll(\Delta\omega_B)^{-1}\approx10^{-7}$ sec. In fact, the lifetime of the vibrational states, which is the delay time of interest, is usually less than 10^{-9} sec. With this simplification, the two terms within curly brackets in Eq. (45) are equal, and the intensity correlation function depends on only a single phonon correlation function. The correlated counting rate G_{12} may be found by integrating Eq. (45) over the sensitive volume and response function of the two detectors. In the notation of Eq. (33), the ensemble average of G_{12} is

$$\langle G_{12}\rangle=\int(1)\int(2)\,\mathrm{Tr}[\rho_B\rho_T$$

$$\times\langle f|\varphi^\dagger(2)\varphi^\dagger(1):\varphi(1)\varphi(2)|f\rangle] . \quad (46)$$

V. TARGET CORRELATIONS

The information about the target correlations is contained in a single phonon correlation function, defined by

$$C_{\mu\lambda\mu'\lambda'}(\mathbf{q}_1\tau_1,\mathbf{q}_2\tau_2)$$

$$\equiv\mathrm{Tr}\{\rho_T[b_{\mu'}(\mathbf{q}_2,\tau_2)b_\mu(\mathbf{q}_1,\tau_1)]_-$$

$$\times[b_\lambda{}^\dagger(\mathbf{q}_1,\tau_1)b_{\lambda'}{}^\dagger(\mathbf{q}_2,\tau_2)]_+\} , \quad (47)$$

where

$$\mathbf{q}_i=\mathbf{p}-\mathbf{k}_i . \quad (48)$$

Although a general evaluation of Eq. (47) is difficult, it is possible to study certain limiting cases. In the harmonic approximation, the phonon Hamiltonian is

$$H_L{}^h=\sum_{\mathbf{q}\lambda}(\hbar\omega_{\mathbf{q}\lambda})[b_\lambda{}^\dagger(\mathbf{q})b_\lambda(\mathbf{q})+\tfrac{1}{2}] , \quad (49)$$

and the time dependence of the phonon operators is given by Eq. (13) as

$$b_\lambda(\mathbf{q},t)=b_\lambda(\mathbf{q})e^{-i\omega_{\mathbf{q}\lambda}t}; \quad b_\lambda{}^\dagger(\mathbf{q},t)=b_\lambda{}^\dagger(\mathbf{q})e^{+i\omega_{\mathbf{q}\lambda}t}. \quad (50)$$

The different vibrational modes in Eq. (49) are uncoupled and undamped. This approximation is therefore unsuitable for the study of lifetime effects.

The phonon correlation function in the harmonic approximation may be calculated with Eq. (50). It is easiest to evaluate the diagonal matrix elements first and then to take the thermal average. The result is

$$C_{\mu\lambda\mu'\lambda'}(\mathbf{q}_1\tau_1,\mathbf{q}_2\tau_2)$$

$$=\langle n_\lambda(\mathbf{q}_1)+1\rangle\langle n_{\lambda'}(\mathbf{q}_2)+1\rangle$$

$$\times\{\delta_{\lambda\mu}\delta_{\lambda'\mu'}+\delta_{\lambda\mu'}\delta_{\lambda'\mu}\delta_{\mathbf{q}_1\mathbf{q}_2}$$

$$\times\exp[i(\omega_{\mathbf{q}_1\lambda}-\omega_{\mathbf{q}_2\lambda'})(\tau_1-\tau_2)]\} . \quad (51)$$

The following property of the thermal averages has been used in the derivation of Eq. (51):

$$\langle n^2\rangle=[\sum_s s^2 e^{-\beta\hbar\omega(s+1/2)}][\sum_s e^{-\beta\hbar\omega(s+1/2)}]^{-1}$$

$$=2\langle n\rangle^2+\langle n\rangle , \quad (52)$$

where

$$\langle n\rangle=(e^{\beta\hbar\omega}-1)^{-1} \quad (53)$$

and β is the usual reciprocal temperature.

The first term on the right side of Eq. (51) represents the uncorrelated portion of C, while the second term contains the true phonon correlations. The factor $\delta_{\mathbf{q}_1\mathbf{q}_2}$ reflects the harmonic approximation, in which the different modes are uncorrelated. The most interesting feature of the correlated portion is the presence of oscillations at the difference frequency of the various modes. For a nonpolar crystal such as diamond, the three optical modes are nearly degenerate for small $\mathbf{q}$, and the oscillations in Eq. (51) have a low frequency.
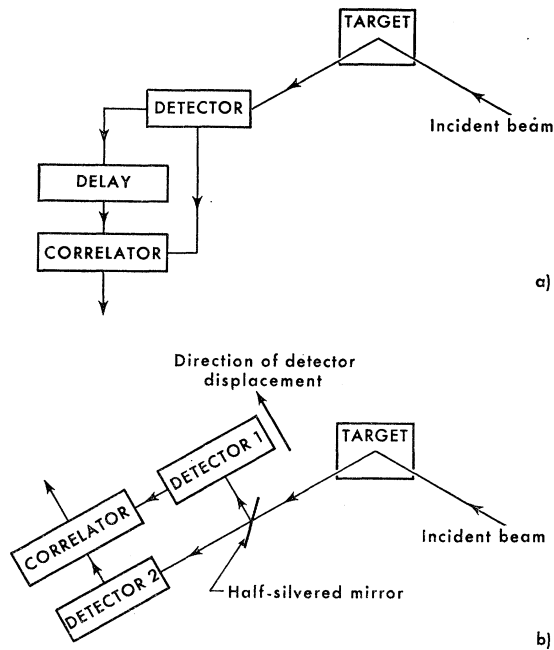
Fig. 3. Apparatus to measure phonon lifetimes with
(a) temporal delay (b) spatial delay.

For a polar crystal such as NaCl, the longitudinal mode lies substantially higher than the transverse modes, and the oscillation frequency is too high to be observed. In a real solid (with anharmonic forces or crystal imperfections), the correlated part of C is damped like $\exp(-\Gamma|\tau_1-\tau_2|)$, and the Kronecker delta in q_1 and q_2 is considerably broadened.

The exponential damping suggests a direct method of measuring phonon lifetimes. If the two detectors in Fig. 1 are replaced by a single detector, as in Fig. 3(a), the correlated counting rate measures the autocorrelation function. As the delay time is increased, the correlated part of C becomes small, providing a measurement of Γ, the inverse lifetime. A second method is shown in Fig. 3(b), where a half-silvered mirror splits the scattered beam. As one detector is moved along the direction of the beam, the damped term again becomes small. Since the phonon lifetimes are very short ($\approx 10^{-9}-10^{-10}$ sec for $T\ll300°K$), the second method is simpler, involving paths of $\approx 10-1$ cm. Unfortunately, the method becomes impractical at room temperatures, when the lifetimes are less than 10^{-11} sec. Phonons in different directions are correlated within a finite solid angle Ω_c; the detector in either Fig. 3(a) or Fig. 3(b) should subtend a solid angle comparable with or less than Ω_c.

In the harmonic approximation, it is possible to evaluate the polarization sums in the calculation of $\langle G_{12}\rangle$. The relevant part of Eq. (45) is

$$\sum_{\lambda\mu\lambda'\mu'}\sum_{\xi\xi'}(R_{\xi\xi'}{}^{\mu'})^*(R_{\xi\xi}{}^{\mu})^*R_{\xi\xi}{}^{\lambda}R_{\xi\xi'}{}^{\lambda'}$$

$$\times C_{\mu\lambda\mu'\lambda'}(q_1\tau_1,q_2\tau_2) . \quad (54)$$

The structure of the Raman tensor for diamond has already been discussed in the evaluation of Eq. (31). With the expression Eq. (51) for the phonon correlation function, Eq. (54) at equal retarded times reduces to

$$|R|^4\langle n_0+1\rangle^2[\{1+\cos^2\chi\ \sin^2\psi_1\}\{1+\cos^2\chi\ \sin^2\psi_2\}$$
$$+\delta_{q_1q_2}\{1+\cos^4\chi\ \sin^4\psi_1\}] , \quad (55)$$

where, as in Fig. 2 and Eq. (31), the incident beam is polarized at an angle χ with respect to the xz plane, and the two photons are scattered through angles ψ_1 and ψ_2 in the same plane.

The phonon correlation function may be treated more generally if $\tau_1=\tau_2$, since the equal-time commutation relations Eq. (3) are then valid. The time ordering becomes unnecessary, and Eq. (47) may be written as

$$C_{\mu\lambda\mu'\lambda'}(q_1\tau,q_2\tau)$$
$$=\delta_{\lambda\mu}\delta_{\lambda'\mu'}\langle[n_\lambda(q_1)+1][n_{\lambda'}(q_2)+1]\rangle , \quad (56)$$

where we have assumed that $q_1\neq q_2$. In the limit of equal times, Eq. (47) thus measures the correlation between the density of phonons with different wave vectors and polarizations. In actual crystals, the phonons have a finite lifetime Γ^{-1}, and are localized within a distance $\Lambda=v_g\Gamma^{-1}$, where v_g is the group velocity. A wave packet of dimension Λ requires a spread $\Delta q\approx\Lambda^{-1}$ in the wave vectors, which means that phonons with wave vectors q_1 and q_2 are correlated if $|q_1-q_2|\lesssim\Lambda^{-1}$. The dispersion curve for optical phonons is very flat, so that v_g and Λ are both small. Hence correlations between phonons persist for widely separated wave vectors.

A possible experiment would measure the variation in correlated counting rate with the angular separation of the two detectors in Fig. 1. The counting rate decreases for angular separations larger than the range of correlations. Equation (56) shows that diamond is not a suitable choice for this technique, because the average number of phonons is much less than one. A better substance would be (for example) GaP, which has a pair of strong first-order Raman lines at an energy of ≈ 400 cm^{-1}.[14] A temperature of 300°K corresponds to a mean occupation number $\langle n\rangle\approx 0.16$, so that correlation measurements would indeed be feasible.

VI. FLUCTUATIONS IN COUNTING RATE

In any actual experiment, the correlated counting rate $\langle G_{12}\rangle$ fluctuates, and it is important to estimate the counting times necessary to achieve a reasonable signal to noise ratio. Measurements of intensity correlations in scattering experiments are usually limited by the low intensity of the scattered beam. As we shall show, however, an intense laser source allows counting times the order of 50 μsec. The fluctuations in $\langle G_{12}\rangle$ have been studied by Goldberger and Watson,[15] and their results are applied in this section.

[14] M. V. Hobden and J. P. Russell, Phys. Letters 13, 39 (1964).
[15] M. L. Goldberger and K. M. Watson (to be published).

It is convenient to define a quantity

$$G_{av}(\tau) \equiv \int_0^T G_{12}(T_1, T_1+\tau) dT_1, \qquad (57)$$

whose ensemble average is

$$\langle G_{av}(\tau) \rangle = T \langle G_{12}(\tau) \rangle, \qquad (58)$$

because the beam intensity is constant during the measurement interval. The fluctuation in the correlated counting rate is determined by

$$\langle G_{av}{}^2 \rangle - \langle G_{av} \rangle^2, \qquad (59)$$

and the signal-to-noise ratio is

$$S/N = \langle G_{av} \rangle \{ \langle G_{av}{}^2 \rangle - \langle G_{av} \rangle^2 \}^{-1/2}. \qquad (60)$$

The form of Eq. (59) depends markedly on the experimental situation. For Raman scattering, the different parts of the crystal radiate in phase, so that the approximation of a "point source" is valid in the calculation of Eq. (59). In addition, the beam spectrum is narrow, in the sense that

$$c \gg w\Delta\omega_B, \quad \Delta\tau_r \Delta\omega_B \ll 1, \qquad (61)$$

where $\Delta\tau_r$ is the response time of the detector. Equation (61) is well satisfied for typical values: $\Delta\tau_r \approx 10^{-10}$ sec, $w \approx 1$ cm, $\Delta\omega_B \approx 10^7$ sec^{-1}.

For our proposed experiments, Eq. (59) is dominated by a single term and is given approximately by[15]

$$\langle G_{av}{}^2 \rangle - \langle G_{av} \rangle^2 \approx 2 \langle G_1 \rangle \langle G_2 \rangle TM, \qquad (62)$$

where the inequality

$$|Y_1 - Y_2 - c(T_1 - T_2)| \ll c(\Delta\omega_B)^{-1} \approx 3 \times 10^3 \text{ cm} \qquad (63)$$

has been assumed. The quantity M may be estimated as

$$M \approx \min\{ (\Delta\tau_r)^{-1}, cw^{-1} \} \approx 10^{10} \text{ sec}^{-1}. \qquad (64)$$

It is most convenient to use a gas laser, which can be made to operate in a single mode; the intensity from such a laser is $\approx 10^{17}$ photons/sec. From Eq. (41), the number of scattered photons per unit solid angle is $\approx 10^{10}$ sec^{-1}, so that $\langle G_1 \rangle \approx \langle G_2 \rangle \approx 10^8$ sec^{-1}, for a solid angle of 10^{-2}. The magnitude of $\langle G_{12} \rangle$ may be estimated from Eqs. (45) and (46) as $2\langle G_1 \rangle \langle G_2 \rangle$, and the signal-to-noise ratio is

$$S/N \approx 2\langle G_1 \rangle \langle G_2 \rangle T \{ 2\langle G_1 \rangle \langle G_2 \rangle T / \Delta\tau_r \}^{-1/2}$$
$$\approx (2T)^{1/2} \times 10^3. \qquad (65)$$

As usual, S/N increases as $T^{1/2}$. Counting times $\approx 5 \times 10^{-5}$ sec are needed to obtain $S/N \approx 10$.

A solid-state laser is not suitable for Raman-scattering experiments (although it is more intense than a gas laser), because it operates in several frequency modes simultaneously. Furthermore, stimulated Raman emission can occur at very high intensities, which would completely obliterate any effects of correlated counting rates.

The technique of measuring target correlations with scattered beams is applicable, in principle, to many different situations. We have shown that a gas laser gives practical counting times (the order of 50 μsec) for intensity correlations with optical phonons. Measurements of photon correlations might also be feasible with other scattering mechanisms, such as acoustical phonons or spin waves.[8]

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