transfer is accompanied by simultaneous rotational transitions of $\Delta J = \pm 1$ in the CO_2 molecule and $\Delta J = 0, \pm 2$ in the N_2 molecule. Since large rotational-energy changes will destroy the resonance of Reaction (1), only the low-lying rotational levels of the CO_2 and N_2 molecules, which are closely spaced, will contribute significantly to the vibration-transfer process, reducing the effective cross section. The temperature dependence will not be strongly affected, however, even though the population of the low-lying levels is inversely proportional to the temperature. This is because higher temperatures correspond to shorter interaction times, τ, allowing greater resonance defects (and therefore higher rotational levels) according to the criterion $|\omega\tau| \lesssim 2$. Calculations are currently in progress which properly account for rotational transitions, and the results will be reported when they are completed.

Above about 1000°K we see that the experimental cross sections increase with temperature. This is in agreement with the theory of Herzfeld,[13] and indicates that above about 1000°K the short-range repulsive forced dominate the vibration-transfer process.

*This research was sponsored by the U. S. Air Force Avionics Laboratory and the Advanced Research Projects Agency under Contract No. AF33(615)-3832.

[1]L. Landau and E. Teller, Physik. Z. Sowjetunion 10, 34 (1936).

[2]K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic Press, Inc., New York, 1959).

[3]C. B. Moore, R. E. Wood, B. L. B. Hu, and J. T. Yardley, J. Chem. Phys. 46, 4222 (1967).

[4]W. A. Rosser, private communication.

[5]R. L. Taylor, M. Camac, and R. M. Feinberg, in Eleventh Symposium on Combustion, Berkeley, California, 1966 (unpublished), p. 49.

[6]Recent experimental data obtained by W. A. Rosser (private communication) indicate a negative temperature dependence above room temperature. Further shock-tube measurements by R. L. Taylor (private communication) also support the negative temperature dependence of the cross section in the range $T \lesssim 1000$°K.

[7]B. H. Mahan, J. Chem. Phys. 46, 98 (1967), has also pointed out that long-range, dipole-dipole interactions dominate exactly resonant energy-transfer processes among infrared-active molecules.

[8]For an axially symmetric charge distribution the only nonvanishing quadrupole moment is

$$Q = Q_{ZZ} \equiv \sum_i q_i (3z_i^2 - r_i^2),$$

where q_i is the ith charge, z_i is the axial coordinate, and $r_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$ is the radius.

[9]A. Messiah, Quantum Mechanics (North-Holland Publishing Company, Amsterdam, The Netherlands, 1962), p. 728.

[10]Bateman Manuscript Project, Table of Integral Transforms, (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I, p. 118.

[11]J. T. Houghton, Proc. Phys. Soc. (London) 91, 439 (1967).

[12]R. K. Nesbet, J. Chem. Phys. 40, 3619 (1964).

[13]K. F. Herzfeld, J. Chem. Phys. 47, 743 (1967).

FREQUENCY-CORRELATION EFFECTS IN CASCADE TRANSITIONS INVOLVING STIMULATED EMISSION

Helen K. Holt
Atomic Physics Division, National Bureau of Standards, Washington, D. C.
(Received 5 July 1967)

In a recent Letter,[1] Cordover, Bonczyk, and Javan report the measurement of the frequency profile of the light emitted in the second part of the cascade process $2s_2 \to 2p_4 \to 1s_4$ in neon. The neon gas was part of a He-Ne laser tuned to the $2s_2 \to 2p_4$ neon transition (1.15 μ). The spontaneously emitted $2p_4 \to 1s_4$ light (0.6096 μ) was viewed along the direction of the laser light propagation and was found to have two bumps superimposed on the Doppler-broadened profile. The bumps were due to light spontaneously emitted by $2p_4$ atoms populated by the laser transition from the $2s_2$ state. The Doppler background was caused by the emission from $2p_4$ atoms populated in other ways, e.g., by electron bombardment or by cascade from higher states.

The shape of the bumps depends on the natural widths of the three states and on the frequencies of the two photons. In an erratum to Ref. 1,[2] the shape of each bump was said to be a Lorentzian of width (full width at half-maximum)

$$\gamma = (\omega_{bc}/\omega_{ab})(\gamma_a + \gamma_b) + (\gamma_b + \gamma_c) \text{ rad/sec}, \quad (1)$$

where $a \to b$ is the laser transition, $b \to c$ is the 0.6096-μ transition, $\hbar\omega_{ab} = E_a - E_b$, $\hbar\omega_{bc} = E_b - E_c$, and $\hbar\gamma_a, \hbar\gamma_b, \hbar\gamma_c$ are the level widths (see Fig. 1). The bump width was measured as a function of pressure and the data extrapolated to zero pressure to obtain a lifetime for the $1s_4$ level. A similar result, with the omission of the second γ_b, was obtained by other workers.[3] The purpose of this Letter is to point out that, although (1) would be correct if there were no correlation between the frequencies of the two photons emitted in the cascade, the inclusion of the correlation gives a different result.

What is meant here by frequency correlation can be understood by considering atoms at rest emitting frequencies ω and ω' successively. ω is distributed as a Lorentzian about ω_{ab} of width $\gamma_a + \gamma_b$, and ω' is centered on ω_{bc} with a width $\gamma_b + \gamma_c$. If the two photons come from the same atom, however, and ω is greater than ω_{ab} by a given amount, ω' will tend to be smaller than ω_{bc} by the same amount so that ω and ω' can add up to $\omega_{ac} = (E_a - E_c)/h$ to within $\gamma_a + \gamma_c$.[4] Thus, the probability that a given frequency be emitted in the transition $b \to c$ depends on the frequency emitted in going from a to b; once ω is specified, the probability distribution of ω' is no longer a Lorentzian about ω_{bc}. The effect is similar to the case of resonance fluorescence when the primary radiation is monochromatic.[5] The emitted line is expected to have the same width as the primary line, rather than the larger natural width.

In the following discussion, I shall attempt to show how the frequency correlation affects the shape of the bumps by first deriving the shape assuming ω and ω' to be independent and then taking into account the correlation between ω and ω'. It is assumed throughout that the natural widths of the levels are much smaller than the Doppler widths, that the laser is operating near threshold in a single mode, and that the pressure is such that collisions do not destroy the correlation. For simplicity, the $2p_4$ state is assumed to be populated by stimulated emission only.

The bumps are caused by the fact that the laser light can interact only with atoms having a small range of values of v_z, velocity along the z axis, and are related to the holes "burned" in the $2s_2$ population distribution as a function of v_z.[6,7] Suppose that the cavity is tuned to a frequency Ω (in rad/sec) which is greater than ω_{ab} by an amount large compared with $\gamma_a + \gamma_b$, but small compared with the Doppler width. To an atom with velocity v_z, the cavity radiation appears to be composed of two running waves, one in the $+z$ direction of frequency $\Omega(1 - v_z/c)$ and one in the $-z$ direction of frequency $\Omega(1 + v_z/c)$. The probability that an atom be stimulated to emit is a Lorentzian function of $\omega - \omega_{ab}$ of width $\gamma_a + \gamma_b$, where ω is the frequency of the stimulating radiation in the rest frame of the atom. Thus, atoms with $\Omega v_z/c \sim (\Omega - \omega_{ab})$, to within $\gamma_a + \gamma_b$, are stimulated to emit by the $+z$ traveling wave, and those with $\Omega v_z/c \sim -(\Omega - \omega_{ab})$ are stimulated to emit by the $-z$ traveling wave. The distribution of velocities of atoms in the $2p_4$ state is such that the quantity $\Omega v_z/c$ is distributed as two Lorentzians, one about $(\Omega - \omega_{ab})$ and one about $-(\Omega - \omega_{ab})$, each of width $\gamma_a + \gamma_b$.

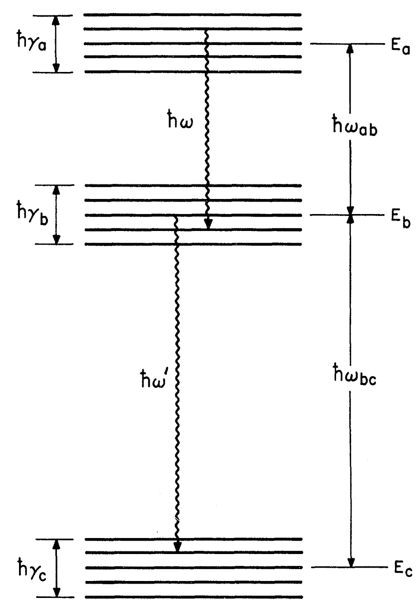

FIG. 1. Schematic energy-level diagram.

Denote the frequency of the photon emitted in the transition $b \to c$ in the rest frame of the atom by ω'. If it is assumed that ω' is independent of the frequency of the first photon ω, then ω' is distributed about ω_{bc} as a Lorentzian of width $\gamma_b + \gamma_c$. In going to the laboratory frame, ω' becomes $\omega_L' = \omega'(1 + v_z/c)$ when the 0.6096-μ light is viewed from the $+z$ direction. Using the result of the preceding paragraph, the quantity $\omega' v_z/c$ is distributed as two Lorentzians about $\pm(\omega'/\Omega)(\Omega - \omega_{ab})$, each of width $(\omega'/\Omega)(\gamma_a + \gamma_b) \cong (\omega_{bc}/\omega_{ab})(\gamma_a + \gamma_b)$. Thus, ω_L' is two

Lorentzians of equal heights about $\omega_{bc} \pm (\omega_{bc}/\omega_{ab})(\Omega-\omega_{ab})$, each of width $(\omega_{bc}/\omega_{ab})(\gamma_a+\gamma_b)+(\gamma_b+\gamma_c)$. This result was obtained by the authors of Ref. 1 in the Erratum to Ref. 1.

In considering the effect of the frequency correlation of the two photons, some simplicity results from taking γ_a and γ_c to be negligible compared with γ_b. Then $\omega+\omega'$ has a sharp value, ω_{ac}, although both ω and ω' can vary over the range γ_b. Consider an atom with a fixed value of v_z. This atom emits only one frequency in the transition $a\to b$: $\omega=\Omega(1-v_z/c)$ for $v_z>0$ or $\omega=\Omega(1+v_z/c)$ for $v_z<0$. Since $\omega+\omega'=\omega_{ac}$, the atom also emits only one frequency in the transition $b\to c$: $\omega'=\omega_{ac}-\omega$. (In the uncorrelated case, for fixed v_z, ω' would be a Lorentzian of width γ_b about ω_{bc}.) The frequency seen in the laboratory frame is $\omega_L'=\omega'(1+v_z/c)$, which is also sharp. In contrast to the uncorrelated case, the entire width of the bumps comes from the sum over v_z. First consider atoms with $v_z>0$. For these atoms, $\omega_L'=[\omega_{ac}-\Omega(1-v_z/c)](1+v_z/c)\cong\omega_{ac}-\Omega+\omega_{ac}v_z/c$. Using the result given above for the distribution of $\Omega v_z/c$, for $v_z>0$, $\omega_{ac}v_z/c$ is distributed about $(\omega_{ac}/\Omega)(\Omega-\omega_{ab})$ with a width $(\omega_{ac}/\Omega)\gamma_b$. Thus, ω_L' is a Lorentzian about $\omega_{ac}-\Omega+(\omega_{ac}/\Omega)(\Omega-\omega_{ab})\cong\omega_{bc}+(\omega_{bc}/\omega_{ab})(\Omega-\omega_{ab})$ of width $(\omega_{ac}/\Omega)\gamma_b\cong(\omega_{bc}/\omega_{ab})\gamma_b+\gamma_b\equiv\gamma_1$. For atoms with $v_z<0$, $\omega_L'=[\omega_{ac}-\Omega(1+v_z/c)](1+v_z/c)\cong\omega_{ac}-\Omega+(\omega_{ac}-2\Omega)(v_z/c)$. The quantity $(\omega_{ac}-2\Omega)(v_z/c)$ is distributed about $-[(\omega_{ac}-2\Omega)/\Omega]\times(\Omega-\omega_{ab})$ with a width $[(\omega_{ac}-2\Omega)/\Omega]\gamma_b$. ω_L' is a Lorentzian about $\omega_{bc}-(\omega_{bc}/\omega_{ab})(\Omega-\omega_{ab})$ of width $[(\omega_{ac}-2\Omega)/\Omega]\gamma_b\cong(\omega_{bc}/\omega_{ab})\gamma_b-\gamma_b\equiv\gamma_2$. Thus, the widths of the bumps should differ by $2\gamma_b$, with the higher frequency bump being the broader; if the laser is tuned to a frequency smaller than ω_{ab}, the lower frequency bump is the broader. Since the areas are equal, the heights of the bumps should also differ. It is assumed here that ω_{bc} is larger than ω_{ab}; if the opposite is true, $\gamma_2=\gamma_b-(\omega_{bc}/\omega_{ab})\gamma_b$. If γ_a and γ_c are not negligible, which is probably the case, the widths become

$$\gamma_1=(\omega_{bc}/\omega_{ab})(\gamma_a+\gamma_b)+\gamma_b+\gamma_c,$$

$$\gamma_2=(\omega_{bc}/\omega_{ab})(\gamma_a+\gamma_b)-\gamma_b+\gamma_c.$$

Although the signal-to-noise ratio was probably too low in the previous experiments[1,3] to permit observation of an unambiguous difference in the bump widths and heights, improvements can be made so that the effect should be observable unless γ_b is too small or the pressure too high. The effect of gas pressure on the shapes is difficult to estimate, since collisions would tend to destroy the correlation but would also destroy the velocity selection which leads to the bumps. In any case, it is not correct to extrapolate high-pressure results to low pressures[1] unless one assumes that γ_b is small compared with γ_a and γ_c. Finally, I should like to point out that a measurement of the bump widths, made in conjunction with a measurement of $\gamma_a+\gamma_b$ from the "Lamb dip,"[8] could yield the values of γ_a, γ_b, and γ_c separately.

I should like to acknowledge useful discussions with Dr. P. J. Bender, who confirmed these results using the density-matrix method, Dr. J. A. White, Dr. W. C. Martin, Jr., Dr. M. M. Birky, and Dr. W. G. Schweitzer, Jr.

[1] R. H. Cordover, P. A. Bonczyk, and A. Javan, Phys. Rev. Letters 18, 730 (1967).

[2] R. H. Cordover, P. A. Bonczyk, and A. Javan, Phys. Rev. Letters 18, 1104 (1967).

[3] W. G. Schweitzer, Jr., M. M. Birky, and J. A. White, to be published.

[4] V. Weisskopf and E. Wigner, Z. Physik 63, 54 (1930).

[5] W. Heitler, The Quantum Theory of Radiation (Oxford University Press, London, England, 1954), 3rd ed., p. 196.

[6] W. R. Bennett, Jr., in Quantum Electronics, Proceedings of the Third International Congress, Paris, 1964, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 441.

[7] A. Szoke and A. Javan, Phys. Rev. 145, 137 (1966).

[8] W. E. Lamb, Jr., Phys. Rev. 134, A1429 (1964).