

**RB-100**

**MOLECULAR AMPLIFICATION  
AND GENERATION OF MICROWAVES**



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## Molecular Amplification And Generation Of Microwaves

This bulletin presents a general introduction to the field of amplification and generation of microwaves using molecular, rather than electronic processes. The basic physical properties of molecular systems as related to amplification are reviewed. The properties of molecular amplifiers, such as gain, bandwidth, saturation power and noise figure are discussed, and several specific types of amplifiers are described. These include the molecular-beam Maser, the "hot-grid cell", amplifiers excited by rf pulses and by "adiabatic fast passage" and amplifiers based on multi-level molecular internal energy systems, including "optically pumped" amplifiers.

Molecular amplifiers may add very little noise to the signal to be amplified; noise figures under one db can be obtained. With suitable feedback, such amplifiers become oscillators of extremely high spectral purity. High gains can be achieved, using regeneration, but bandwidths are relatively small. These range from the order of tens of kilocycles, for amplifiers using a gaseous molecular system, to megacycles, using solids. Molecular amplifiers saturate at low input powers, of the order of microwatts. Variations of the devices discussed may provide a means of generating millimeter and sub-millimeter waves.

### Introduction

In familiar microwave devices, such as klystrons, magnetrons and traveling-wave tubes, dc power is converted to microwave power by the interaction of moving charged particles (electrons) with a microwave field. Microwave fields can also interact with *uncharged* matter (molecules). In such "molecular interaction", there is no flow of charge, with its kinetic or positional energy being transformed to rf energy, but instead the *internal* energy of molecules is *directly* converted to microwave energy. This is a familiar process at very short wavelengths, for example, emission of visible light from a gas discharge. This light represents the direct transformation of internal electronic excitation energy of *neutral* atoms to electromagnetic radiation energy. However, there is a difference between such optical radiation and the microwave radiation of interest in this bulletin that is of profound importance. Atoms excited in a discharge tube have a very strong tendency to radiate light spontaneously. The presence of similar radiating atoms nearby has negligible effect on the emission and the atoms emit independently of each other in an *incoherent* fashion. In the microwave frequency region such spontaneous emission of internal energy as radiation is relatively unimportant. Molecules must be *induced* to give up their internal energy by locating them

in a microwave field that either is generated by neighboring radiating molecules or is externally applied; this induced emission is *coherent*, that is, phase-related to the general radiation field.

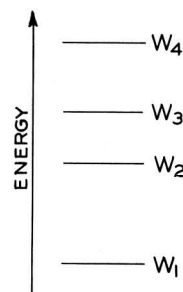


Fig. 1 - Schematic representation of energy states (or levels).

The motions of electrons in atoms and molecules are such that the associated energies form a discrete set, that is, only those motions leading to certain *allowed* internal energies can exist. Thus, the internal energy associated with the motion of electrons bound in molecules is quantized; an electron can only exist in certain *energy states*. It has become conventional to indicate the scheme of energy states for a molecule by a diagram such as Fig. 1. From this representation the term *energy level* has arisen, and is used interchangeably with *energy state*.



The vibrational energies of atoms bound together in molecules and molecular rotational energies are similarly quantized and may also be represented by an energy level diagram. Other sources of internal energy, such as the orientation of molecular (and nuclear) dipole moments in an applied electric or magnetic field, are also quantized.

The various internal energy states corresponding to different excitations of electronic motion generally lie a few electron-volts apart. Molecular vibrational energies are much smaller, typically of the order of  $10^{-3}$  electron-volts; rotational energies are even lower, in the  $10^{-4}$  to  $10^{-5}$  electron-volt range, as are orientational energies of paramagnetic ions in usual laboratory magnetic fields (a few thousand gauss). Nuclear moments are about three orders of magnitude weaker yet, corresponding to energies of only about  $10^{-7}$  electron-volts.

Molecules in certain of their energy states can interact with a microwave radiation field of appropriate frequency and either absorb energy from the radiation field while jumping to a state of greater internal energy, or, under the influence of the radiation field, can give up some of their internal energy and drop to a state of lower energy. The amount of internal energy thus transferred, i.e., the difference in energy of the two energy levels,  $W_1 - W_2$ , is linearly related to the frequency of the radiation field:

$$W_1 - W_2 = h\nu$$

Here  $h$  is Planck's constant and  $\nu$  is the frequency. VHF fields (at about 100 mc) correspond to energy differences of only about  $4 \times 10^{-7}$  electron-volts. These can therefore produce nuclear magnetic resonance, that is, they can interact with molecules to change the orientation of nuclear magnetic moments in fields of a few thousand gauss. Microwave frequencies of about 10 kmc correspond to energies of about  $4 \times 10^{-5}$  electron-volts, which are typical of rotational and electronic paramagnetic energies. Visible light, as mentioned earlier, corresponds to the relatively large energy associated with changes of electronic motion- al energies (a few electron-volts). Because of the very small energy transfers associated with low frequencies, useful molecular amplifiers are more likely to operate at frequencies above 1000 mc.

Consider two energy levels of a molecule whose energy difference corresponds to a microwave frequency. If a molecule in the lower energy state is placed in a microwave field of this frequency, it will absorb energy and hop to the upper state. An atom in the upper state, on the other hand, will give up energy to the microwave field and drop to the lower level. The probability for both transitions is the same. Therefore, whether a system of many molecules exhibits a *net* absorption or emission of energy depends on whether more molecules are in the lower or upper energy state. All molecular systems when allowed

to come to thermal equilibrium have more molecules in the lower of each pair of states, and hence are absorptive. However, it is possible to build devices that will disturb the molecular system and put it in an emissive condition where more molecules are in the upper of a pair of states. Such a disturbed, emissive system is a "molecular amplifier": a microwave field incident on it will take up energy from the molecules. By providing suitable feedback, a "molecular oscillator" can be made.

Several methods of producing an emissive condition have been devised. One that has been tested is the molecular-beam Maser,<sup>1,2</sup> in which a beam of ammonia molecules is physically separated into two beams, one consisting of upper-state molecules and the other of lower-state molecules. The upper-state beam is then used in a resonant cavity as the emissive molecular system of a microwave amplifier. As an oscillator the beam Maser has exceedingly high spectral purity; as an amplifier it has only a very narrow amplification bandwidth.

Another device, the "hot-grid cell", also uses ammonia gas. However, unlike the beam Maser, this is a "sealed off" gas system that does not require continuous pumping. An emissive state is maintained by selective reflection of upper-state molecules at one wall. In addition to the advantage of eliminating pumps, the amplification bandwidth is an order of magnitude larger than in the beam-type Maser. It is still only tens of kilocycles, however.

To get greater bandwidths without loss of gain, molecular systems of higher density are needed. It is expected that megacycle bandwidths can be attained using solids. Two methods of exciting such systems by interchanging the populations of two levels have been found. These are: a) excitation by applying a short controlled pulse of microwave power at the transition frequency, and b) excitation by "adiabatic fast passage", where a strong exciting microwave field is swept in frequency past the transition frequency. However, these excitation methods are essentially pulsed ones, giving only intermittent amplification. Another method of exciting a solid molecular system that operates continuously has been developed. In this, a strong microwave field equalizes the populations of two energy states and amplification is secured at a lower frequency by inducing transitions between one of these two levels and an intermediate undisturbed level.

<sup>1</sup> J. P. Gordon, H. J. Zeiger and C. H. Townes, "The Maser - New Type of Microwave Amplifier, Frequency Standard and Spectrometer", *Phys. Rev.*, vol. 99, pp. 1264-1274, August 15, 1955.

<sup>2</sup> The term "Maser", an acronym for "microwave amplification by stimulated emission of radiation", has been coined to describe the general class of microwave amplifiers based on molecular interaction. It is often used in a more restricted sense to refer to one form of molecular amplifier, that using a beam of excited molecules.

Whereas conventional tubes require dc power to operate, all of these methods of exciting solid systems entail the supplying of energy to the system at microwave frequencies. In a solid, the life-time of an excited state during which it can interact with radiation is determined in part by thermal motions of the lattice atoms. Therefore, solid state devices seem to work best at very low (liquid helium) temperatures; this practical disadvantage will probably be overcome by future developments of materials in which interactions with the lattice are very weak.

A very narrow band gaseous amplifier that is excited, not with microwave energy but with visible light is also being worked on. This should provide, as does the molecular beam Maser, a tuned element of exceedingly high  $Q$  for an "atomic clock" or frequency standard.

There are two basic features of molecular amplification and generation that make it attractive in comparison to electronic devices. First, molecular amplification does not have many of the sources of noise that plague electronic amplification, such as flicker noise, induced grid noise, shot noise and partition noise.<sup>3,4</sup> Molecular

amplifiers can therefore have low noise figures and molecular oscillators can have high spectral purity. Second, the frequencies are determined by the internal molecular structure. Therefore, the limitations on the generation of very short microwaves imposed by electron transit time effects of conventional tubes no longer restrict the attainable frequencies. Of the disadvantages of molecular amplifiers, the narrow amplification bandwidth is perhaps the most serious.

Section II of this bulletin gives a general discussion of the basic physical processes involved in emissive molecular systems and of the requisite molecular properties. Those who are familiar with the basic concepts in the interaction of microwaves with matter will wish to skip over this section. The specific requirements for amplification and oscillation are discussed in Section III; Section IV discusses in detail the practical approaches to the subject outlined earlier. A discussion of the present state of the art and comments on possible future developments in Section V conclude the bulletin.

## II. Basic Physical Properties and Processes of Molecular Systems

### A. Description of a Single Molecule

Numerous experiments have shown that an isolated molecule cannot have arbitrary internal energy, but can have only one of a *discrete* number of energies: that is, molecular internal energies are *quantized*. This behavior is in contrast to that of a free electron, whose kinetic energy, or potential energy in an electric field, can assume any of a continuous range of values.<sup>5</sup> Molecules and electrons may therefore be expected to have basically different types of interaction with electromagnetic radiation. To study molecular interactions, the properties of molecules in the various internal energy states must be known.

According to quantum theory, the state of a molecule is completely specified by a *state function*. Any general

state of a molecule can be expressed by a linear combination of the state functions that describe the individual quantized energy states. Denote the function corresponding to the state with internal energy  $W_i$  by  $\psi_i$ ; then any general state  $\psi$  can be expressed by:

$$\psi = \sum_i a_i \psi_i . \quad (1)$$

The  $a_i$ 's, which may be complex, are analogous to Fourier coefficients in a Fourier decomposition, and are called "probability amplitudes". They have the physical significance that if the internal energy is measured, the probability that the value  $W_i$  will be obtained is equal to  $|a_i|^2$ . Eq. (1) has the interpretation that unless  $a_i = 0$  for  $i \neq j$  and  $|a_j| = 1$ , the energy of the system is *uncertain*: an energy measurement may yield *any* of the values  $W_i$  for which  $a_i \neq 0$ . A state describable by such a state function is called a *superposition* energy state, as it is made up of a linear combination of pure energy states  $\psi_i$ . In predicting the result of an energy measurement, only the *magnitude* of the  $a_i$ 's is important. Other properties of the system in a superposition state, however, such as its interaction with microwaves, depend on the relative *phases* of the various  $a_i$ 's, as well as on their magnitudes.

<sup>3</sup> J. R. Pierce, "Physical Sources of Noise", *Proc. IRE*, vol. 44, pp. 601-608, May, 1956.

<sup>4</sup> J. L. Lawson and G. E. Uhlenbeck, *THRESHOLD SIGNALS*, McGraw-Hill Book Co., New York, 1950.

<sup>5</sup> The kinetic energy and any positional potential energy of a molecule are similarly unquantized. However, we are considering only "molecular interactions", where changes of internal, rather than kinetic (or positional) energy are involved.

There are certain processes that do not change the energy of the molecule, but produce changes in these relative phases; the interaction process between molecules and radiation is critically dependent on such processes.

### B. Description of Many-Molecule Systems

Thus far, only isolated single molecules have been considered. When a number of such molecules are assembled, the interaction between these elements may be weak, or sporadic. In either case, the system of individual-molecule energy levels may still be used, with the aid of statistical methods, to predict the behavior of the many-molecule macrosystem. On the other hand, in cases where the interactions are continuous and strong, the individual-molecule energy level scheme breaks down and must be replaced by one treating the macrosystem as a whole. It is systems with weak or intermittent interactions between the elements which will be of interest in this bulletin. Even in a solid, molecular systems that are but weakly coupled to each other and their surroundings may be found. Certain paramagnetic ions, introduced as impurities in a host crystal lattice, are examples.

Consider a system of many molecules. If the internal energy of one of the molecules is measured, it will be found to be one of the discrete allowed values. The question arises: what can be said about the distribution of the molecules among these allowed energy states? The answer given by statistics is the following. If the system is in thermal equilibrium at an (absolute) temperature  $T$ , in any sample containing many molecules the ratio of the number of molecules with energy  $W_1$  to the number of molecules with energy  $W_2$  is given by:

$$\frac{N(W_1)}{N(W_2)} = \frac{N_1}{N_2} = \exp\left(-\frac{(W_1 - W_2)}{kT}\right) \quad (2)$$

where  $k = 1.38 \times 10^{-16}$  erg/ $^{\circ}$ K, ( $1.38 \times 10^{-23}$  joule/ $^{\circ}$ K,) is Boltzmann's constant. This Boltzmann distribution has the properties that states of lower energy are more highly populated than states of higher energy and that the population ratio of any two states can be enhanced by lowering the temperature and reduced by raising it.

### C. Relaxation Effects

The Boltzmann distribution of molecules among the various possible energy states is an *equilibrium* one; that is, as long as the temperature of the system is held constant, once this distribution is attained, it will remain the same indefinitely.<sup>6</sup> Any distribution whatever, if it is

<sup>6</sup>It thus must correspond to a state of maximum entropy, or maximum disorder.

left undisturbed for a sufficient length of time, will spontaneously change until it is an equilibrium one. The processes that produce such changes in an arbitrary distribution are known as the "relaxation mechanisms". Interaction with a "black-body" radiation field, collisions between molecules, and electric and magnetic dipolar interactions between molecules are among such processes of importance in molecular amplifiers.

For convenience in handling many problems, the relaxation processes are divided into two not necessarily mutually exclusive classes. These correspond to the two different ways a system can deviate from equilibrium. Once the total number of molecules in each energy state is known, the total internal energy  $W$  of the molecular system is given by

$$W = \sum_i N_i(W_i) \times W_i.$$

If the total energy of the molecular system differs from its thermal equilibrium value  $W_{eq}$ , spontaneous changes will occur that result in a net transfer of energy between the internal degrees of freedom of the molecular system and its surroundings (a heat reservoir). Those processes that contribute to this exchange of energy are called "longitudinal" relaxation processes. In many cases of practical importance, the displacement of the molecular internal energy  $W$  from its equilibrium value  $W_{eq}$  decreases exponentially with time:

$$\frac{d(W - W_{eq})}{dt} = -\frac{1}{T_1} (W - W_{eq}).$$

The reciprocal of the decay constant, which has the dimensions of a time, is known as the "longitudinal" (or "spin-lattice") relaxation time. It is conventionally designated  $T_1$ .<sup>7</sup>

There is another kind of relaxation process. Since the equilibrium state is one of complete randomness or molecular chaos (maximum entropy), any coherence or definite phase relationship between the various molecules constituting the system corresponds to a (partially) ordered, and hence non-equilibrium state. In this case, the energy of the system  $W$  need not depart from its equilibrium value

<sup>7</sup>The reader is warned of the possible confusion of the absolute temperature,  $T$ , and the relaxation times  $T_1$  (and  $T_2$ ). This symbology has become standard in the field, and hence is retained here. It arose in the field of nuclear magnetic resonance, where the internal energy is the magnetic dipolar or "spin" orientation energy of nuclei in an applied magnetic field. The term "spin-lattice" relaxation also arose in nuclear magnetic resonance, where the crystal lattice constitutes the heat reservoir.

$W_{eq}$  to produce a non-equilibrium state. Relaxation processes that tend to destroy such order in the system are known as "transverse" processes, and where they can be adequately described by an exponential decay of the order are describable phenomenologically by a "transverse" (or "spin-spin") relaxation time  $T_2$ . Examples of this type of relaxation process can be found that either a) can simultaneously transfer energy between the system and surroundings, or b) can involve only members of the system itself, and hence cannot exchange energy with the heat reservoir. A collision between two gas molecules, where internal energy can be transformed to kinetic energy of the molecules is an example of the former; the magnetic dipolar interaction between two localized spins in a crystal is an example of the latter.

#### D. Molecular Interaction with a Radiation Field

A molecule can exchange energy with an oscillating electromagnetic field only if the frequency of the oscillation is related to the allowed internal energies of the molecule by the Bohr frequency condition

$$W_i - W_j = h\nu \quad (3)$$

where  $W_i$ ,  $W_j$  are the internal energies of the  $i$ th and  $j$ th quantum states,  $\nu$  is the frequency of the radiation and  $h = 6.624 \times 10^{-27}$  erg-sec ( $6.624 \times 10^{-34}$  joule-sec) is Planck's constant. The energy in a monochromatic electromagnetic wave is also quantized; that is, the energy in the wave comes in "packets", or *photons*, and can only change in finite steps corresponding to the energy of a photon. For a wave of frequency  $\nu$ , the energy of the photons is just  $h\nu$ . The interaction may then be considered to be either one of two processes, the absorption of a photon by the molecule with a corresponding increase in internal energy, or the emission of a photon with a corresponding drop in internal energy. With this picture the above frequency condition (Eq. (3)) follows immediately from the principle of conservation of energy. The apparent discrepancy between a quantized radiation field of discrete photons and the continuously variable electric and magnetic fields usually dealt with can be resolved by considering the size of a photon. For a microwave frequency of 10 kmc, the photon energy is only  $6.6 \times 10^{-17}$  erg ( $6.6 \times 10^{-24}$  joule); a wave at this frequency carrying a microwatt of power has a flux of  $1.5 \times 10^{17}$  photons/sec. It is because ordinary practice deals with such huge numbers of photons that the discreteness of the wave energies does not generally make itself manifest.<sup>8</sup>

There are three basic types of radiation field-molecule interaction: absorption, induced or stimulated emission, and spontaneous emission. In absorption, as the name implies, a photon is absorbed by the molecule, which is then lifted to a state of higher energy. Induced emission is the reverse process, whereby, under the action of an applied electromagnetic field, a molecule emits a photon at the frequency of the applied field and drops to a lower internal energy level. In spontaneous emission, a molecule in an excited energy state, i.e., an energy state other than the lowest, even though it is undisturbed by an applied field, emits a photon at the characteristic frequency given by the Bohr frequency condition and drops to a lower energy state. These types of interaction were treated on a phenomenological basis by Einstein<sup>9</sup> before an adequate microscopic quantum picture was available. His "B-coefficient" gives the probability for either absorption or induced emission; his "A-coefficient" gives the spontaneous emission probability. In amplification, we are clearly dealing with induced emission. In the case of a molecular microwave generator, the basic process is *coherent* spontaneous emission. This can alternatively be considered a case of self-induced stimulated emission, where the energy supplying the inducing field comes from the molecular system itself.

It is not possible to cause transitions between every two internal energy states by means of electromagnetic radiation. In addition to the conservation of energy requirement given by Eq. (3), momentum conservation and other requirements must be met. The effect of this is to impose restrictions on what pairs of states may be coupled by radiation. These restrictions are known as "selection rules", and are usually expressed in terms of allowed changes in the quantum numbers specifying the internal states. For example, the rotational energy of a simple diatomic molecule may be written as

$$W_J = BJ(J + 1)$$

where  $B$  is a constant depending on the molecule and  $J$  is the rotational quantum number. The usual selection rule

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questions dealing with the "wave-particle duality" of radiation are too involved to go into here. The interested reader is referred to texts on quantum theory for further discussion, e.g., David Bohm, QUANTUM THEORY, Prentice-Hall, Inc., New York, N. Y., 1951, Chapters 1 and 2, or W. Heitler, THE QUANTUM THEORY OF RADIATION, University Press, Oxford, England, 2nd Edition, 1950.

<sup>9</sup> A. Einstein, "On the Quanta Theory of Radiation" *Phys. Zeit.*, vol. 18, pp. 121-128, March 15, 1917. For a brief review of Einstein's argument, see: E. U. Condon and G. H. Shortley, THE THEORY OF ATOMIC SPECTRA, Cambridge University Press, Cambridge, Eng., 1951, Chapter IV.

<sup>8</sup> The question of the meaning of *phase* when a radiation field is considered to consist of particle-like photons, and other



for transitions between the states of energy  $W_J$  is given by

$$\Delta J = J_{final} - J_{initial} = \pm 1,$$

i.e., the rotational quantum number must change by one unit when a photon is emitted or absorbed, the plus sign corresponding to absorption, the minus to emission. This is because each photon carries one unit of angular momentum, which must be conserved.

A very important point about absorption and emission must be made. Both a microscopic quantum mechanical treatment and Einstein's phenomenological treatment give the result that, for a given applied microwave field strength, the probability of a molecule in the lower of two energy states absorbing a photon is exactly equal to the probability of a molecule in the upper of the same two states giving out a photon by induced emission. This has the consequence that any macrosystem that is in a state where two energy levels are equally populated will be completely transparent to radiation at the frequency corresponding to their energy difference. Neglecting the usually insignificant spontaneous emission effects, it is only an imbalance in populations that produces an observable effect. For computational purposes it is therefore possible, when considering transitions of molecules between two energy levels, to "pair off" the molecules as far as possible, and to deal only with the "excess" molecules in the more highly populated state.

To make this somewhat clearer, consider a gas in thermal equilibrium. Since radiation at only one frequency will be of interest, only the two states coupled by radiation at this frequency need be considered. Let the upper energy state be designated (2), the lower (1); let there be a total of  $N$  molecules in these two states.

$$N_1 + N_2 = N.$$

From Eq. (2),

$$\frac{N_2}{N_1} = \exp \left[ -\frac{W_2 - W_1}{kT} \right] = \exp \left[ -\frac{h\nu}{kT} \right]. \quad (4)$$

Solving these equations for  $N_1$  and  $N_2$  gives

$$N_1 = \frac{N}{1 + \exp \left( -\frac{h\nu}{kT} \right)},$$

$$N_2 = \frac{\exp \left( -\frac{h\nu}{kT} \right) N}{1 + \exp \left( -\frac{h\nu}{kT} \right)}$$

"Pairing off" molecules, the "excess population" is

$$N_1 - N_2 = N \tanh \left( \frac{h\nu}{2kT} \right) \quad (5a)$$

At microwave frequencies,  $\frac{h\nu}{2kT} \ll 1$  generally holds, and Eq. (5a) becomes

$$N_1 - N_2 \approx \frac{h\nu}{2kT} N. \quad (5b)$$

(At extremely low temperatures, the exact Eq. (5a) must be used.) If radiation at frequency  $\nu$  is incident on the gas, it will absorb energy (since  $N_1 > N_2$ ) at the same rate as a gas composed of  $\frac{h\nu}{2kT} N$  molecules all of which are in the lower of the two energy states.

It has been seen that an electromagnetic field of the proper frequency can induce transitions between the energy levels. It must be remembered, however, that while this is going on, the relaxation mechanisms are operative, tending to restore the system to thermal equilibrium. For weak transition-inducing fields, the relaxation mechanisms are strong enough to maintain the system in an absorptive state not much different from that of thermal equilibrium. However, if the electromagnetic field strength is increased, molecules tend to undergo induced transitions to the upper energy state faster than the relaxation processes can restore them to the lower state. The effective "pairing off" of molecules is then shifted from that at equilibrium, and there are fewer molecules now in the "excess" to absorb. The total absorbed power does not decrease, as the power absorption per molecule is greater at higher fields. It does reach a limit, however, determined by the maximum rate that the relaxation processes can remove the internal energy from the molecular system thus supplied by the microwave field. Under these conditions, the microwave absorption is said to be "saturated". An analogous situation will be encountered in considering amplification.

The above discussion has assumed that the energy levels are perfectly sharp; that is, that only one (monochromatic) frequency couples two energy levels. This is not strictly true: transitions may be induced by a band of frequencies centered at the frequency given by Eq. (3). Thus, absorption or emission spectral "lines" have a



finite frequency width, which can be ascribed to a "width" of the corresponding energy levels. The physical reason for this width is that because of relaxation processes, a molecule interacts with the radiation field for only a finite time before it is "dephased" and (effectively) the interaction stops momentarily. But in an interaction time  $\sim T_2$ , a molecule will "see" essentially the same number of cycles of the microwave field as long as the frequency lies in a band of frequencies of width  $\Delta\nu \approx 1/T_2$ . In other words, a molecule is not able to tell what frequency is acting on it to within a range  $\Delta\nu$  in the time  $T_2$  before the interaction is interrupted. The spectral width of a molecular resonance should thus be given by  $\Delta\nu T_2 \approx 1$ , with short relaxation times leading to broad lines and conversely. This is as observed: in a gas, where  $1/T_2$  is proportional to the pressure, the observed line width is also proportional to the pressure. Dephasing processes not describable by a relaxation time  $T_2$ , such as the Doppler effect, have a similar result. Such effects are commonly met with in the microwave spectroscopy of gases and provide a means of studying molecular interaction processes in detail.<sup>10,11</sup> In a solid, where the molecules are very near to each other, strong interactions, leading to short relaxation times, are frequently encountered. Resonances in solid systems are thus apt to cover a broad band of frequencies. (Resonances of over a hundred megacycles are generally too broad to use for amplification purposes, but widths roughly one megacycle and up can be found.)

In some cases it happens that certain frequencies couple more than one pair of states. This may happen because two or more internal states correspond to the same energy, (degeneracy), or because two or more pairs of levels "accidentally" are separated by the same energy gap. The first of these cases is the more common. However, in many systems of interest neither effect occurs. To simplify the discussion, it will be assumed that neither occurs in all the following. It is a good approximation to ignore the effects of all energy states but the two that are directly coupled. This reduces the situation to a relatively simple two-state case.

### E. Properties of a Two-State System

In the case that only two energy levels are of importance, one deals with a system of molecules that interacts with the radiation field only when the frequency

of the field is near the resonant frequency  $\nu_0$ . Such a radiation field induces transitions between the two energy states, molecules in the lower state undergoing transitions that absorb energy from the radiation field and lift them to the upper energy state, and molecules in the upper energy state giving up energy to the field and dropping to the lower state. As mentioned earlier, the transition probability for an atom in the lower state to absorb a photon and jump to the upper state is exactly equal to that for an atom in the upper state to emit a photon and jump to the lower state, (neglecting the usually small spontaneous emission effects). A semi-quantum mechanical calculation of these transition probabilities is given in the Appendix. The basic result of interest here is that if a molecule is in either one of the energy states at time  $t = 0$ , at time  $t$  the probability that it has undergone a transition and is in the other state is given by:

$$\text{Transition Probability} = \frac{\frac{pE}{b}^2}{(\nu - \nu_0)^2 + \left(\frac{pE}{b}\right)^2} \sin^2 \left\{ \pi \left[ (\nu - \nu_0)^2 + \left(\frac{pE}{b}\right)^2 \right]^{1/2} t \right\} \quad (6)$$

A dipole transition has been assumed, with  $p$  the molecular electric dipole moment and  $E$  the amplitude of the applied microwave field. (Although the electric case has been assumed, all expressions are equally valid if  $E$  is replaced by a microwave magnetic field  $H$ <sup>12</sup> if  $p$  is then taken as the *magnetic* dipole moment.)  $\nu$  is the frequency of the applied field and  $\nu_0 = (W_2 - W_1)/h$ . Eq. (6) is plotted in Fig. 2; as shown there, the transition probability oscillates between zero and

$$\frac{\left(\frac{pE}{b}\right)^2}{(\nu - \nu_0)^2 + \left(\frac{pE}{b}\right)^2}$$

On resonance, ( $\nu = \nu_0$ ), a molecule oscillates between the two states, while somewhat off resonance, a molecule that starts in one state never quite gets to the other (with certainty) before the process is reversed.

The average power flow to or from the radiation field due to transitions depends on a suitable averaging of transition probabilities, the averaging being dependent on the physical situation envisioned. One important case is that of collisions randomly distributed in time determin-

<sup>10</sup> W. Gordy, W. V. Smith and R. F. Trambarulo, MICROWAVE SPECTROSCOPY, John Wiley and Sons, Inc., New York, N. Y., 1953.

<sup>11</sup> C. H. Townes and A. L. Schawlow, MICROWAVE SPECTROSCOPY, McGraw-Hill Book Company, Inc., New York, N. Y., 1955.

<sup>12</sup> Strictly speaking,  $B$  should be used instead of  $H$  for the microwave field. Common usage in the field, however, replaces  $B$  with  $H$ ; to avoid confusion with the literature,  $H$  will be used throughout this report.

ing the interaction period. From Eq. (6), the instantaneous rate of energy transfer is

$$P(t) = P(t - t_1) = h\nu_0 \times \frac{d}{dt}(\text{Transition probability}) = \frac{\pi b\nu_0 \left(\frac{pE}{h}\right)^2}{\left[(\nu - \nu_0)^2 + \left(\frac{pE}{h}\right)^2\right]^{1/2}} \sin \left\{ 2\pi \left[ (\nu - \nu_0)^2 + \left(\frac{pE}{h}\right)^2 \right]^{1/2} (t - t_1) \right\}. \quad (7)$$

Here the last interruptive collision occurred at time  $t_1$ . The probability that a molecule had its last collision between times  $t_1$  and  $t_1 + dt_1$  is given by

$$\frac{1}{T_2} \exp \left[ -\frac{(t - t_1)}{T_2} \right] dt_1 .$$

The average power is found by averaging Eq. (7) over this distribution of times  $t_1$ :

$$P_{avg} = \int_{-\infty}^t P(t - t_1) \frac{1}{T_2} \exp \left[ -\frac{(t - t_1)}{T_2} \right] dt_1$$

$$P_{avg} = \frac{b\nu}{2T_2} \left(\frac{pE}{h}\right)^2 \frac{1}{(\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2 + \left(\frac{pE}{h}\right)^2}$$

The above averaging over collision times implicitly assumes that  $T_1 = T_2$ . A calculation made under the assumption of  $T_1 \neq T_2$  gives the more general result

$$P_{avg} = \frac{b\nu}{2T_2} \left(\frac{pE}{h}\right)^2 \frac{1}{(\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2 + \frac{T_1}{T_2} \left(\frac{pE}{h}\right)^2}. \quad (8)$$

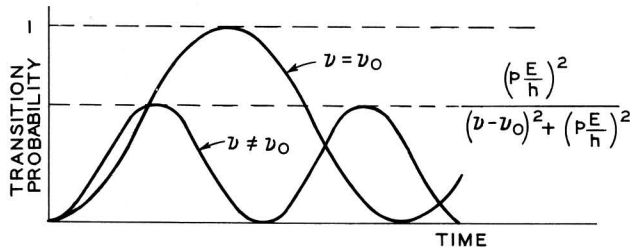


Fig. 2 - Transition probabilities between energy states as a function of time for molecules initially in one of two microwave-coupled states when subjected to microwave radiation at or near the resonant frequency.

This is the often-observed Lorentz line shape shown in Fig. 3. From the last factor in Eq. (8) it is seen that the power is roughly independent of the frequency as long as

$$(\nu - \nu_0)^2 \ll \left(\frac{1}{2\pi T_2}\right)^2 + \frac{T_1}{T_2} \left(\frac{pE}{h}\right)^2 ,$$

while it drops off rapidly with increasing departure from resonance in the range

$$(\nu - \nu_0)^2 \gg \left(\frac{1}{2\pi T_2}\right)^2 + \frac{T_1}{T_2} \left(\frac{pE}{h}\right)^2 .$$

The frequency bandwidth for interaction is thus approximately given by

$$(\nu - \nu_0)^2 \approx \left(\frac{1}{2\pi T_2}\right)^2 + \frac{T_1}{T_2} \left(\frac{pE}{h}\right)^2. \quad (9)$$

This illustrates a general feature common to all physical situations: for short transverse relaxation times  $T_2$ , the

AVERAGE POWER FLOW BETWEEN MOLECULES AND RADIATION FIELD.

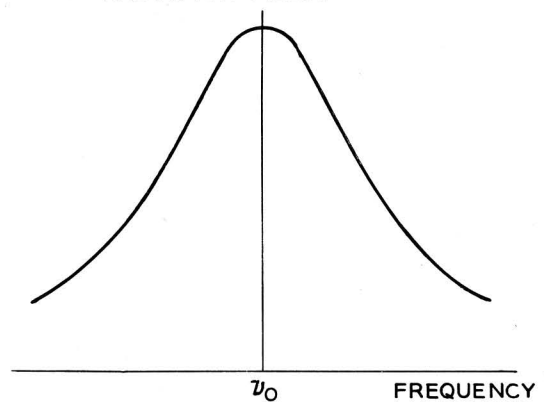


Fig. 3 - Average power transferred between molecules and a microwave field at frequencies near resonance, showing the often-observed Lorentz shape.

interaction is spread over a broad band of frequencies, and conversely, and for high microwave field strengths, the interaction frequency width is similarly (saturation) broadened.

With a different physical situation, such as in a device employing a beam of molecules where the interaction time is the time for the beam to traverse the device, the time averaging is different from the above and the resulting line shape is non-Lorentz. The basic ideas and general results are the same whatever the proper averaging, however.

#### F. Classical Treatment

The foregoing has been a semi-quantum-mechanical *microscopic* approach, where the results of experiments with a large number of molecules were deduced on the basis of what happens to individual molecules. In most cases of interest for amplification, only the gross *macroscopic* behavior is important, and all results can be obtained on a phenomenological basis using a purely classical treatment.

The connection between the microscopic and a macroscopic treatment is easily seen in the case of a system of electron spins in a magnetic field, for example. The elementary dipoles can exist in only two energy states, corresponding to alignment roughly along and against the field. As seen from Eq. (5b), at thermal equilibrium the excess number of spins in the lower energy state, leading to alignment with the field, is given by

$$N_1 - N_2 = \frac{h\nu}{2kT} N .$$

Now, however,

$$h\nu = 2\mu H ,$$

where  $\mu$  is the magnitude of the component of an elementary dipole along the field, so that

$$N_1 - N_2 = \frac{N\mu}{kT} H .$$

The macroscopic magnetic moment is given by

$$M = \mu(N_1 - N_2) = \frac{N\mu^2}{kT} H .$$

From this, a static magnetic susceptibility  $\chi_0$  can be defined by

$$M = \chi_0 H ,$$

with

$$\chi_0 = \frac{N\mu^2}{kT} .$$

(The discrepancy by a factor of 3 between this and the classical Langevin formula is apparent rather than real:  $\mu$  is the field-parallel component of the total dipole moment  $\mu_0$ , and it can be shown quantum mechanically that  $\mu_0 = \sqrt{3} \mu$ .)

The macroscopic moment  $\vec{M}$  is parallel and proportional to the total angular momentum  $\vec{A}$  of the system.

$$\vec{M} = \gamma \vec{A} .$$

$\gamma$  is known as the *gyromagnetic ratio* of the system. The classical relation between the torque applied to a system possessing angular momentum and the rate of change of the angular momentum then gives the dynamic behavior of the molecular system.

$$\frac{d\vec{A}}{dt} = \text{Torque} = (\vec{M} \times \vec{H})$$

$$\frac{d\vec{M}}{dt} = \gamma (\vec{M} \times \vec{H})$$

or

$$\frac{dM_x}{dt} = \gamma (M_y H_z - M_z H_y)$$

$$\frac{dM_y}{dt} = \gamma (M_z H_x - M_x H_z)$$

$$\frac{dM_z}{dt} = \gamma (M_x H_y - M_y H_x) .$$

Take the direction of the (assumed large) static magnetic field along the z-axis and assume that the microwave magnetic fields are in the x-y plane. The spin energy

of the system is then given by

$$\frac{dM_y}{dt} = \gamma (M_z H_x - M_x H_z) - \frac{1}{T_2} M_y$$

$$W = -M_z H_z,$$

$$\frac{dM_z}{dt} = \gamma (M_x H_y - M_y H_x) - \frac{1}{T_1} (M_z - M_{eq}).$$

with a thermal equilibrium value of

$$W_{eq} = -M_{eq} H_z.$$

If the effects of relaxation processes are included in the above equations, they become

$$\frac{dM_x}{dt} = \gamma (M_y H_z - M_z H_y) - \frac{1}{T_2} M_x$$

These are the famous equations first introduced by Bloch<sup>13</sup> to explain the phenomena of nuclear magnetic resonance.

Similar classical treatments can be given for the molecular amplification systems discussed later in this bulletin, by introducing a *complex* electric or magnetic microwave susceptibility, the imaginary part corresponding to the absorption (or emission) of energy by the molecular system and the real part to the molecularly-induced dispersion. In general, however, the *microscopic* approach will be used herein as it gives a better detailed picture of the processes occurring.

### III. Basic Amplifier and Oscillator Relations

In the preceding section, a discussion of the basic physical processes of importance in dealing with microwave amplification using the molecular interaction between matter and radiation was given. These ideas will now be applied to the microwave amplification or generation process itself, in particular, to the possible time-dependence of gain, the power handling capabilities, the available gain, the amplification bandwidth, the noise figure and the efficiency of molecular amplifiers.

#### A. Continuous and Pulse Operation

The excitation process of the molecular system during which it is put into an emissive condition, i.e., one in which there are more molecules in the upper of two microwave-coupled energy states, inevitably interferes with the amplification or oscillation process. Thus, if all molecules in the system are excited simultaneously only pulse operation<sup>14</sup> is possible, and each useful period of

amplification or oscillation must be followed by a "dead" period while the system undergoes excitation. To achieve continuous operation, the various molecules constituting the macrosystem must undergo excitation at different times. The excitation process can occur either in the same region as the amplification process, or the molecules can be excited outside the interaction region and then brought into the amplification region. Each of the above possibilities is used in one or more of the devices to be discussed later.

In all molecular devices, both amplifiers and oscillators, power losses in the microwave structures are of great importance. To have an amplifier (or oscillator), it is essential that more power be transferred to the field from the molecular system than is lost (to resistive heating) in the structure. In a pulsed system, the state of the macrosystem is a function of time, and hence whether or not this condition for amplification is satisfied may also be time-dependent.

#### B. Saturation

As seen above (Eq. (8)) for absorption, (it is also true for emission,) the transfer of energy to the radiation

<sup>14</sup> A point of terminology arises here. It is always possible to gate a continuous amplifier (or oscillator) off and on, thereby achieving intermittent or "pulsed" operation. In this report, however, the term "pulse operation" will not refer to such "gated continuous operation" but only to systems where the energy transfer to the field is intrinsically intermittent due to the mode of excitation.

<sup>13</sup> F. Bloch, "Nuclear Induction", *Phys. Rev.*, vol. 70, pp. 460-474, October 1, 1946.

field is proportional to the incident power, and hence the amplification is linear, as long as

$$\frac{T_1}{T_2} \left( \frac{pE}{b} \right)^2 \ll \left( \frac{1}{2\pi T_2} \right)^2$$

or

$$E \ll \frac{b}{2\pi p (T_1 T_2)^{1/2}} \quad (10)$$

Physically, linear amplification is only obtained when but a small fraction of the total available energy in a molecular system is extracted by induced emission. Thus, unless the strength of the transition-inducing microwave field satisfies the above condition, the amplifier will be operating in a non-linear (saturated) fashion. As seen from Eq. (9), the frequency bandwidth for interaction (with no saturation) is related to the relaxation time by

$$(\text{Molecular bandwidth}) \lesssim \frac{1}{\pi T_2}$$

Therefore, the condition for linearity of amplification is

$$E \ll \frac{b}{2p} \left( \frac{T_1}{T_2} \right)^{1/2} \times (\text{Molecular bandwidth}).$$

For electric dipole transitions, such as are common in a gaseous system,  $p$  is of the order of  $10^{-18}$  esu<sup>15</sup> ( $1.6 \times 10^{-29}$  coulomb-meters); for magnetic dipole transitions, as would be found in a paramagnetic amplifier,  $p$  is about  $10^{-20}$  emu ( $10^{-23}$  joule-meter<sup>2</sup>/weber). Thus, for linear amplification, the microwave fields must satisfy the conditions:

$$\begin{aligned} E (\text{electric dipole}) &\ll 3 \times 10^{-9} \left( \frac{T_1}{T_2} \right)^{1/2} \\ &\times (\text{Molecular bandwidth}) \text{ stat-volts/cm} \\ &\ll 10^{-4} \left( \frac{T_1}{T_2} \right)^{1/2} \\ &\times (\text{Molecular bandwidth}) \text{ volts/meter} \end{aligned}$$

$$\begin{aligned} H (\text{magnetic dipole}) &\ll 3 \times 10^{-7} \left( \frac{T_1}{T_2} \right)^{1/2} \\ &\times (\text{Molecular bandwidth}) \text{ gauss} \\ &\ll 3 \times 10^{-11} \left( \frac{T_1}{T_2} \right)^{1/2} \\ &\times (\text{Molecular bandwidth}) \text{ webers/meter}^2. \end{aligned} \quad (11)$$

These conditions for linearity can be related to power flow into a cavity amplifier. For a solid-state (paramagnetic) amplifier at 10 kmc, for a bandwidth of 1 mc and  $T_1 = T_2$ , the microwave magnetic field strength in the cavity must be much less than a gauss. This corresponds to an input power much less than a watt. As the example chosen represents a type of molecular amplifier that is relatively difficult to saturate, it is clear that low power handling capabilities should be expected in molecular amplifiers.

### C. Gain

In considering the gain obtainable from a molecular amplifier, the physical situation must again be considered. A rough estimate for a cw amplifier consisting of a waveguide containing molecules in an emissive condition will first be given. For such an amplifier the molecules must have a proper phase relationship with the signal field or they will absorb rather than emit energy. Proper phasing can be assured by bringing the molecules into interaction with the signal field in the pure energy state  $\psi_2$ , corresponding to molecules in the upper energy level, rather than in a superposition energy state. Assuming that the signal to be amplified is on resonance,  $\nu = \nu_0$ , and is weak enough to avoid saturation effects, the average power emitted by each molecule is, from Eq. (8),

$$P = \frac{2\pi^2 \nu p^2 E^2 T_2}{b} \quad (12)$$

If  $N$  molecules contribute to the emission process, the total power is

$$P_{\text{total}} = \frac{2\pi^2 N \nu p^2 E^2 T_2}{b}$$

The incident power in a waveguide is of the order of

$$P_{\text{inc}} = \frac{cAE^2}{8\pi}$$

<sup>15</sup>Gaussian units are used throughout this bulletin, i.e., cgs electrostatic units (esu) for electric quantities and cgs electromagnetic units (emu) for magnetic quantities. This choice is made to conform with conventional usage in the literature of this field, where gaussian units are almost invariably used.



where  $c$  is the velocity of light and  $A$  the cross-sectional guide area. Since the power gain in an infinitesimal length of amplifier is proportional to the incident power, the wave will grow exponentially as it travels down the guide, past the emitting molecules. The gain can thus be written neglecting guide attenuation, as

$$\text{Gain} = \exp(a \ell)$$

where  $\ell$  is the length of the amplifier and the gain coefficient  $a$  is given by:

$$a = \frac{P_{\text{emitted/cm}}}{P_{\text{incident}}} \quad (13)$$

$$\approx \frac{16\pi^3 \nu p^2 T_2 N_0}{bcA}$$

Here  $N_0$  is the number of molecules per unit length contributing to the emission, that is, in the upper state "excess". Under realizable conditions, (for example, in the "hot-grid cell" discussed later),  $a$  may be of the order of  $10^{-3}$  to  $10^{-4}$  cm $^{-1}$ . Thus, to get a gain of ten, an amplifier length of several meters is required.

Physically, Eq. (13) can be understood as follows. The gain increases with  $\nu$ , as the energy given up by each interacting molecule (the "size" of each photon) is proportional to the frequency. Stronger coupling between the radiation field and the molecules as determined by the dipole moment  $p$  also results in higher gain, as does increased "excess population" of emissive molecules  $N_0$ . Finally, the longer the time  $T_2$  a molecule interacts with the radiation field before it is disturbed, the greater the probability of its giving up its available internal energy as a photon and thus contributing to the amplification.

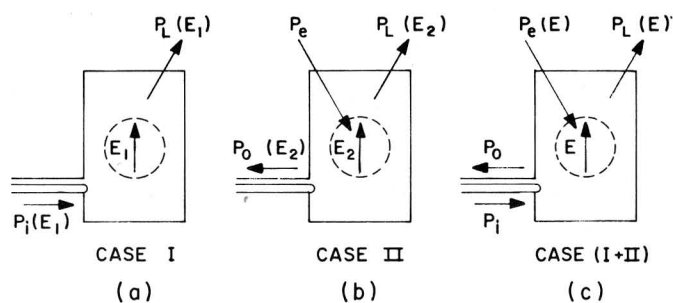


Fig. 4 - Power and field relations in a matched reaction cavity amplifier. (a) A wave is incident on the cavity, building up an oscillating field  $E_1$  in the cavity and being dissipated in resistive losses at the cavity walls. (b) An oscillating magnetization supplies power  $P_e$  in the cavity, building up a field  $E_2$  and producing an outgoing wave,  $P_o$ . (c) The two cases are superposed.

To avoid the practical difficulties associated with a long amplifier, a resonant structure such as a cavity that provides a long effective electrical path in a physically short length may be employed. If the molecular system is located in a resonant cavity, positive feedback is automatically built into the amplifier. It is well known that the gain of such a regenerative amplifier can be arbitrarily large, becoming infinite at the threshold of oscillation. The actual situation may comprise a transmission cavity or a reaction cavity, with arbitrary couplings. A case particularly easy to analyse that displays many of the features of interest is that of a reaction cavity matched to the transmission line, (Fig. 4). The output of the amplifier will be defined as the power leaving the cavity, and the input as the incident power. The behavior of such an amplifier can be seen in the following way.

Consider two situations:

I. Power  $P_i$  is incident on the cavity, which contains the molecular system, but the molecular interaction is effectively "turned off" by shifting the interaction frequency, (e.g., by "detuning" with a Stark<sup>16</sup> or Zeeman field). A resonant field of strength  $E_1$  at the molecular system is built up in the cavity, and there are wall losses  $P_L$ . Since the cavity is matched, there is no outgoing wave. (See Fig. 4a). In this case

$$P_i = P_L = \frac{\nu V \overline{E_1^2}}{4Q_0} \quad (14)$$

where  $\overline{E_1^2}$  is the cavity field squared averaged over the cavity,

$$\overline{E_1^2} = k_0 E_1^2, \quad (15)$$

$V$  is the cavity volume and  $Q_0$  is the unloaded cavity  $Q$ .  $k_0$  is related to the "filling factor".

II. In this situation there is no incident wave, but the molecular system in the cavity is supplying energy to the field, setting up an oscillating field  $E_2$ . Now there is an outgoing wave  $P_o$  and wall losses  $P_L(E_2)$ . (See Fig. 4b). These are related to  $E_2$  by

$$P_o = P_L = \frac{\nu V \overline{E_2^2}}{4Q_0} \quad (16)$$

<sup>16</sup>The shift in the energy of a molecular state due to an applied electric field is known as the Stark effect, after its discoverer. A similar shift of an energy level in a magnetic field is known as the Zeeman effect.

Let  $P_e$  be the power emitted by the molecular system. Then

$$P_e = P_0 + P_L.$$

Finally, superpose the two configurations so that the fields  $E_1$  and  $E_2$  are in phase. (Fig. 4c). Conservation of energy requires that

$$P_i + P_e = P_0 + P_L$$

$P_e$  and  $P_L$  are functions of the total field  $E = E_1 + E_2$  in the cavity, whereas  $P_i$  is related only to the part  $E_1$  and  $P_0$  to the part  $E_2$ :

$$P_i(E_1) + P_e(E) = P_0(E_2) + P_L(E) \quad (17)$$

$$\text{But } P_i(E_1) = \frac{k_0 \nu V}{4Q_0} E_1^2$$

$$P_0(E_2) = \frac{k_0 \nu V}{4Q_0} E_2^2$$

from Eqs (14), (15) and (16), while

$$P_L(E) = \frac{k_0 \nu V}{4Q_0} E^2.$$

To make the discussion definite, assume  $P_e$  has the Lorentz form given by Eq. (8):

$$P_e(E) = \frac{k_1 E^2}{(\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2 + \left(\frac{pE}{b}\right)^2} \quad (18)$$

$$\text{Defining } D \equiv \frac{k_0 \nu V}{4Q_0} \left(\frac{b}{p}\right)^2 \left[ (\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2 \right]$$

$$S \equiv \frac{k_1 b^2}{p^2}$$

$$e_i \equiv \frac{\left(\frac{p}{b}\right)}{\left[ (\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2 \right]^{1/2}} E_i,$$

the conservation-of-energy equation becomes

$$D e_1^2 + \frac{S e^2}{1 + e^2} = D e_2^2 + D e^2.$$

Defining further an "oscillation parameter"  $L$ :

$$L \equiv \frac{S}{2D} \\ \equiv \frac{2k_1 Q_0}{k_0 \nu V \left[ (\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2 \right]}$$

the equation becomes, using  $e = e_1 + e_2$ ,

$$e^3 - e_1 e^2 + (1 - L) e - e_1 = 0 \quad (19)$$

Solutions of this equation, giving  $e$ , and hence  $e_2$ , as a function of  $e_1$  for a fixed value of  $L$  can be easily, if tediously, found. The gain of the amplifier is given by

$$\text{Gain} = \frac{E_2^2}{E_1^2} = \frac{e_2^2}{e_1^2}$$

Gain as a function of input power (actually  $e_1^2$ ) is plotted in Fig. 5 for various  $L$ ; output power ( $e_2^2$ ) is plotted against input power ( $e_1^2$ ) in Fig. 6. Consideration of these figures shows that the optimal operating condition is with low  $e_1$ , (no saturation). In this limit, the gain is

$$\text{Gain (no saturation)} = \frac{L^2}{(1 - L)^2}. \quad (20)$$

When there is no incident power, Eq. (19) becomes

$$e^3 + (1 - L) e = 0$$

with the solutions  $e = 0$  and  $e^2 = L - 1$ . For  $L < 1$ , the second solution is meaningless. However, for  $L > 1$ , a finite real field can exist in the cavity, i.e., oscillations can be sustained. Thus it is appropriate to call  $L$  the "oscillation parameter". The figures clearly show the

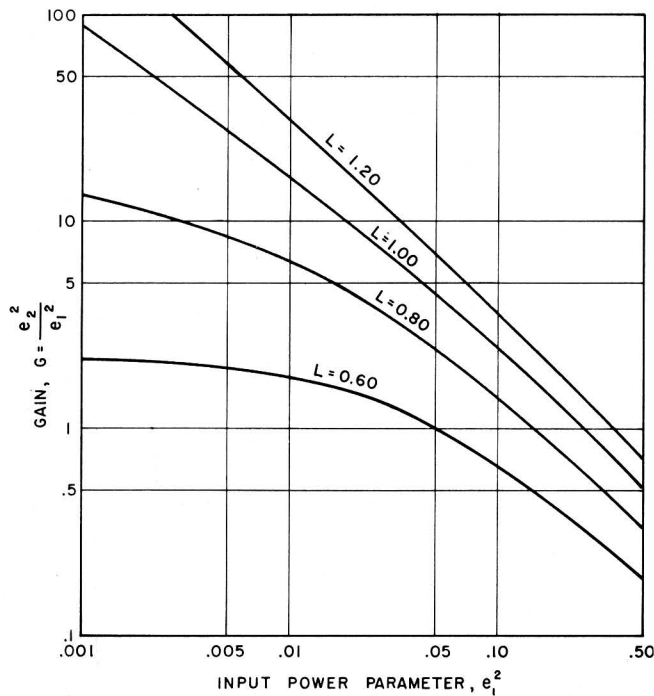


Fig. 5 - Gain versus input power parameter  $e_1^2$  for various values of oscillation parameter  $L$  for a matched reaction cavity amplifier.  $L$  is the ratio of power supplied by the (unsaturated) molecular system to twice the power lost resistively at the walls.

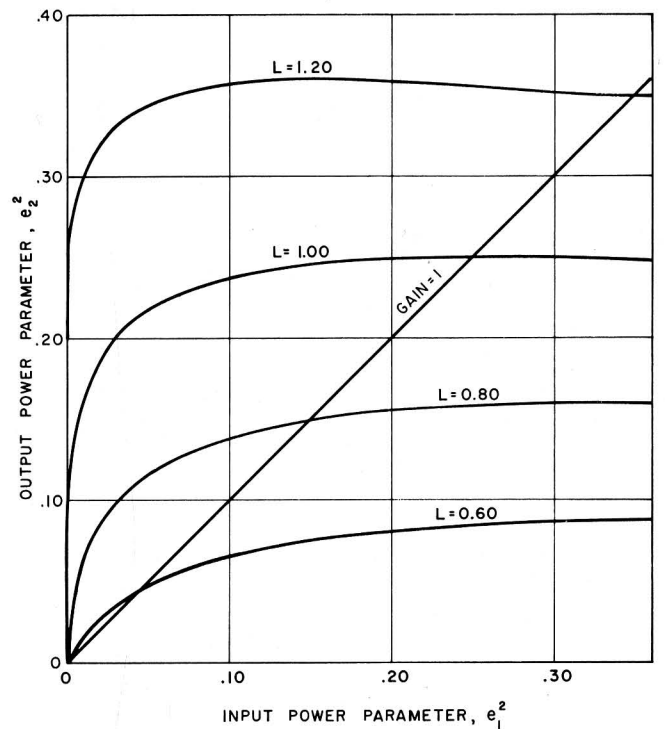


Fig. 6 - Output power parameter  $e_2^2$  versus input power parameter  $e_1^2$  for various values of oscillation parameter  $L$  for a matched reaction cavity amplifier.

saturation behavior at high incident fields where the gain falls off, eventually becoming less than one when the power supplied by the molecular system is unable to compensate for the large wall losses associated with the large cavity fields due to the large input wave. Eq. (20) for low power level gain shows the characteristic increase in gain (to infinity) as the oscillation parameter is increased to one.

It is similarly possible to analyse the case of a transmission cavity with arbitrary coupling, but this general case is mathematically rather unwieldy. Similarly, the details, but not the general picture, will be changed for a physical situation giving a relationship between molecularly emitted power  $P_e$  and microwave field strength  $E$  differing from Eq. (18).

#### D. Bandwidth

Two factors influence the amplification bandwidth: the molecular relaxation processes and the microwave structure. (It is possible, of course, that the latter will also determine the former.) The relaxation processes determine what might be called the molecular bandwidth, which is the width of the resonance line as observed in ordinary absorptive spectroscopy. This width has been discussed earlier in Section II. The actual amplifier will have a somewhat narrower bandwidth, however.

To see this, consider the case of a non-resonant waveguide amplifier with a Lorentz molecular band-shape;

$$\text{Gain} = \exp(a\delta)$$

$$\text{and } a = \frac{\text{const.}}{(\nu - \nu_0)^2 + \left(\frac{1}{2\pi T_2}\right)^2}$$

Defining the bandwidth as the frequency interval between the points where the gain is one-half its maximum value, it is readily shown that

(Amplification bandwidth)

$$\begin{aligned} &= \left[ \frac{\ln 2}{\frac{\ln(\text{Gain})_{\max}}{2}} \right]^{1/2} \frac{1}{\pi T_2} \\ &= \left[ \frac{\ln 2}{\frac{\ln(\text{Gain})_{\max}}{2}} \right]^{1/2} \times (\text{Molecular bandwidth}). \end{aligned}$$

Similarly, for the case of a matched-cavity amplifier with a Lorentz-type resonance, from

$$\text{Gain} = \frac{L^2}{(1-L)^2}$$

and the oscillation parameter  $L$ ,

$$L = \frac{\text{const.}}{(\nu - \nu_0)^2 + \frac{1}{(2\pi T_2)^2}},$$

assuming high gain, i.e.,  $L \approx 1$ , it can be shown that

(Amplification bandwidth)

$$\begin{aligned} &= \frac{(\sqrt{2} - 1)^{1/2}}{(\text{Gain})^{1/4}} \times (\text{Molecular bandwidth}) \\ &= \frac{0.644}{(\text{Gain})^{1/4}} \times (\text{Molecular bandwidth}). \end{aligned}$$

The above expressions show that the gain-bandwidth product is not constant, but increases with increasing gain. For reasonable gains, ( $10 \leq \text{Gain} \leq 100$ ), bandwidths between one-fifth and two-thirds the "molecular width" may be expected.

One of the greatest limitations on molecular amplifiers is the difficulty of getting useful bandwidths. From the discussion of Section II, the molecular bandwidth is inversely proportional to the relaxation time. Eq. (13) shows that the gain increases with frequency, dipole moment, relaxation time and density of "active" molecules. If the bandwidth is increased by shortening the relaxation (or interaction) time in some way, the gain will fall off unless there are compensating changes in either frequency, dipole moment or molecular density. The possible range of these parameters must thus be considered.

In an amplifier where the molecular system is gaseous, electric dipole transitions, which are much stronger than magnetic dipole transitions, can be used. However, dipole moments are of the order of  $10^{-18}$  esu ( $1.6 \times 10^{-29}$  coulomb-meters) whatever the gas used; varying the gas molecule used will not appreciably alter  $p$ . It might be thought that if in a gas amplifier gas collisions are the dominant relaxation mechanisms, any desired bandwidth

could be achieved by increasing the density, since  $T_2 N_0$  is independent of pressure. ( $T_2 \sim 1/N_0$ , so bandwidth  $\sim N_0$ ). In theory this is so; in practice, excitation mechanisms fail to work at high gas pressures. This at present provides an upper limit to expected bandwidths of under 100 kc. Some improvement can be expected by going to molecular resonances at higher frequencies. However, increased losses in the associated microwave circuits tend to reduce the gain obtained in this way.

Another possible way of increasing bandwidth is to use solid (or liquid) molecular systems, with their huge increases in density over gaseous systems. This can compensate for the gain lost by spreading the molecular emission energy over a greater range of frequencies, and greater bandwidths can be obtained this way; however, there are important counterbalancing effects to be considered. One is that in condensed systems magnetic dipole transitions must be used, as the strong, rapidly fluctuating electric fields encountered in liquids and solids relax electric dipole-coupled systems so rapidly that they cannot be excited with presently-available techniques. The largest magnetic dipoles found are of the order of a Bohr magnetron, or  $10^{-20}$  emu ( $10^{-23}$  joule-meter<sup>2</sup>/weber). Since the dipole moment enters as the square, whereas the relaxation time enters only as the first power in the gain coefficient expression (Eq. (13)), a density increase of  $10^4$  is required just to counterbalance the effects of the weaker dipole moment.

Even with magnetic dipoles, relaxation times may be unusably short. At present, paramagnetic materials seem the most promising, the paramagnetism arising from unpaired electron spins. The energy levels determining the resonance frequency are generally in this case associated with the Zeeman energy of the two possible spin orientations with respect to an external applied magnetic field. The transition frequency is given by

$$\nu = \frac{g\mu_B H}{h} \equiv \gamma H.$$

Here  $g$  is the spectroscopic splitting factor and  $\mu_B = 9.27 \times 10^{-21}$  erg/gauss ( $9.27 \times 10^{-24}$  joule-meter<sup>2</sup>/weber) is the Bohr magneton. For paramagnetic spin systems with usable relaxation times,  $g \approx 2$ . This gives a frequency of

$$\nu = 2.8 H \text{ mc}$$

where  $H$  is in gauss.<sup>17</sup> To avoid seriously broadening the

<sup>17</sup> It should be noted that nuclear magnetic moments could in principle be used instead of electronic moments. However, the  $\gamma$ 's corresponding to nuclear moments are two to three orders of magnitude smaller than the electronic  $\gamma = 2.8$  mc/gauss, and thus magnetic fields in the  $10^5 - 10^6$  gauss range are necessary to put the transition frequency in the microwave range.

resonance by magnetic field inhomogeneities, it is necessary to have a field uniform over the sample to a fraction of a percent of the total field. An additional advantage of a paramagnetic amplifier over a gaseous one is that the frequency is readily controllable by means of the applied magnetic field.

### E. Noise Figure

It was pointed out in the Introduction that one of the important properties of molecular amplification is that it can introduce very little additional noise onto a signal. To see this, an expression for the noise figure of a waveguide-type of molecular amplifier will now be derived. Other discussions of molecular amplifier noise have been given in the literature.<sup>1, 18</sup>

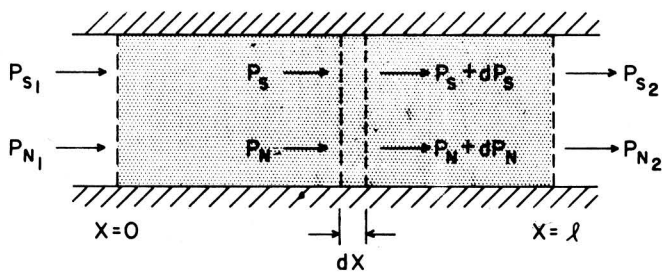


Fig. 7 - Signal and noise powers in a waveguide amplifier.

Referring to Fig. 7, let  $P_S$  be the signal power in a wave traveling to the right at position  $x$ , and  $P_N$  the corresponding noise power (in a unit frequency band about the frequency of  $P_S$ ). In a length of amplifier  $dx$ , the increase in signal power  $dP_S$  is given by

$$dP_S = (N_2 - N_1) \Gamma P_S dx - a_g P_S dx. \quad (21)$$

Here  $N_2$  is the number of molecules in the upper energy state per unit length,  $N_1$  the number in the lower state per unit length,  $a_g$  is the waveguide attenuation coefficient, and  $\Gamma$  is a constant depending on the dipole matrix element for the transition and the guide geometry and mode. The first term on the right-hand side of Eq. (21) represents the molecular amplification (increase in signal power due to excess of stimulated emission over absorption) and the second the reduction in signal power due to resistive losses in the walls.

A similar expression can be written for the increment of noise power:

$$(22)$$

$$dP_N = (N_2 - N_1) \Gamma P_N dx - a_g P_N dx + a_g P_{N_o} dx + \beta N_2 dx.$$

The first two terms on the right here are exactly analogous to the terms in the signal power expression. There are two additional terms, however. The first of these,  $a_g P_{N_o} dx$ , represents black-body radiation from the walls. The subscript "o" refers to a condition of thermal equilibrium at the wall temperature  $T_o$ , taken to be room temperature. The second additional term,  $\beta N_2 dx$ , represents the effects of spontaneous incoherent emission: it is proportional to the number of molecules in the upper energy state. (The proportionality constant  $\beta$ , like  $\Gamma$ , depends on the dipole moment and guide geometry.)

The relationship between  $\beta$  and  $\Gamma$  can be determined by considering the special condition of thermal equilibrium. Then  $dP_N = 0$ , and Eq. (22) becomes

$$0 = (N_{2o} - N_{1o}) \Gamma P_{N_o} dx - a_g P_{N_o} dx + a_g P_{N_o} dx + \beta N_{2o} dx$$

or

$$\beta = \left( \frac{N_{1o}}{N_{2o}} - 1 \right) \Gamma P_{N_o}.$$

But  $N_{2o}/N_{1o} = \exp(-h\nu/kT_o)$ , from Eq. (4), and the Planck distribution law for black-body radiation gives

$$P_{N_o} = \frac{h\nu}{\exp\left(\frac{h\nu}{kT_o}\right) - 1}.$$

From these is obtained the relationship between  $\beta$  and  $\Gamma$ :

$$\beta = h\nu \Gamma.$$

Rewriting Eq. (22) using this relation gives

$$dP_N = [(N_2 - N_1) \Gamma - a_g] P_N dx + (h\nu \Gamma N_2 + a_g P_{N_o}) dx.$$

This can be directly integrated to give

$$\frac{P_{N_2} + \frac{h\nu \Gamma N_2 + a_g P_{N_o}}{(N_2 - N_1) \Gamma - a_g}}{P_{N_1} + \frac{h\nu \Gamma N_2 + a_g P_{N_o}}{(N_2 - N_1) \Gamma - a_g}} = \exp \{ [(N_2 - N_1) \Gamma - a_g] l \}$$

<sup>18</sup>K. Shimoda, H. Takahasi and C. H. Townes, "Fluctuations in Amplification of Quanta", (to be published).



where  $P_{N_2}$  is the noise power out of the amplifier,  $P_{N_1}$  the noise power input and  $\ell$  is the amplifier length. Similarly integrating Eq. (21) for the signal power, the power gain is

$$\text{Gain} = \frac{P_{S_2}}{P_{S_1}} = \exp \{[(N_2 - N_1)\Gamma - a_g]\ell\}.$$

The gain may be written as

$$\text{Gain} = \exp [(a - a_g)\ell]$$

where  $a$  is the "gain coefficient".

Define

$$M \equiv \frac{b\nu\Gamma N_2 + a_g P_{N_0}}{(N_2 - N_1)\Gamma - a_g}.$$

Then

$$G \equiv G = \frac{P_{N_2} + M}{P_{N_1} + M}$$

or

$$\frac{P_{N_2}}{P_{N_1}} = G + (G - 1) \frac{M}{P_{N_1}}.$$

The noise figure  $F$  of the amplifier is defined by

$$F \equiv \frac{P_{N_2}}{G P_{N_1}} \quad \text{for} \quad P_{N_1} = P_{N_0}.$$

$$\text{Thus,} \quad F = 1 + \left(1 - \frac{1}{G}\right) \frac{M}{P_{N_0}}.$$

$M$  can be put in the form

$$M = \frac{b\nu}{1 - \frac{N_1}{N_2}} \left(1 + \frac{a_g}{a - a_g}\right) + \frac{a_g P_{N_0}}{a - a_g}$$

and

$$F = 1 + \left(1 - \frac{1}{G}\right) \left[ \frac{b\nu}{P_{N_0}} \frac{\left(1 + \frac{a_g}{a - a_g}\right)}{\left(1 - \frac{N_1}{N_2}\right)} + \frac{a_g}{a - a_g} \right]$$

In the case  $G \gg 1$ , this can be factored into two terms:

$$F = \left[1 + \frac{N_2}{N_2 - N_1} \frac{b\nu}{P_{N_0}}\right] \left[1 + \frac{a_g}{a - a_g}\right]. \quad (23)$$

The first term on the right is the contribution to the noise figure due to spontaneous incoherent emission, the second the contribution of the effects of black body radiation in the guide. The two terms are closely related, however, as the gain coefficient  $a$  and the term  $N_2/(N_2 - N_1)$  both depend on the "excess population" in the upper state produced by the excitation process. This expression also shows clearly that losses are vitally important: unless  $a \gg a_g$ , the amplifier will have a poor noise figure. It is also clear that a large class of "paired off" molecules adversely affects the noise figure by increasing  $N_2$  without increasing  $N_2 - N_1$ . However, if the gain coefficient  $a$  greatly exceeds the attenuation coefficient  $a_g$  and there are few molecules  $N_1$  in the lower state,

$$F \approx 1 + \frac{b\nu}{P_{N_0}} \approx 1 + \frac{b\nu}{kT_0}$$

which is of the order of 1.004, or a noise figure of 0.02 db.

#### F. Efficiency

In general, the efficiency of molecular amplifiers is low. If the overall efficiency is defined as the ratio of the increase of microwave power in the amplifier to the total power expended in associated electronic circuits, etc., as well as in the molecular system, the efficiency is invariably low, (well under one percent). The reasons for this vary with the different means of exciting the molecular systems, and hence can only be properly discussed in connection with an excitation method. However, a few general considerations will indicate that high efficiency is not to be looked for in molecular amplifiers.

Roughly speaking, energy must be supplied to each molecule at a rate given by

$$P_{in} \approx \frac{b\nu}{T_1}$$

where  $\nu$  is the amplification frequency. The power transferred to the radiation field from the molecular system is, from Eq. (12),

$$P_{out} \approx \frac{2\pi^2\nu p^2 E^2 T_2}{b}$$

The efficiency is thus of the order of

$$\text{Efficiency} = \frac{P_{out}}{P_{in}} \approx 2\pi^2 T_1 T_2 \left( \frac{pE}{b} \right)^2 .$$

The condition for linear amplification is that (Eq. 10)

$$\left( \frac{pE}{b} \right)^2 \ll \frac{1}{4\pi^2 T_1 T_2} .$$

So

$$\text{Efficiency} \ll 1/2 .$$

From this it is seen that the requirement of linear amplification severely limits the efficiency that can be expected.

#### IV. Practical Approaches

Having discussed molecular amplifiers in general, various devices that apply the idea of emissive molecular interaction to solve the practical problems of low-noise amplification, the generation of microwaves and production of frequency standards of high constancy ("atomic clocks") will now be considered.

##### A. Molecular-Beam Maser

The various devices developed as molecular amplifiers differ mainly in the way in which an emissive condition is obtained. A discussion of amplifiers in a sense thus becomes a discussion of excitation methods. One well-known type of molecular amplifier is the ammonia-beam Maser.<sup>1, 19</sup> Here the excitation method consists of physically separating a beam of gas molecules into two beams, one containing the lower state and one the upper state emissive molecules. After the separation, the emissive beam is used in an amplifier cavity.

The Maser is shown schematically in Fig. 8a. The gas molecules issue from the source (a chamber maintained at an ammonia pressure of a few millimeters of mercury) as a well-collimated beam, the directivity being obtained by means of a source opening consisting of channels which are long compared to their diameter and short compared to the mean free path of the gas. This beam travels first through a focuser, (Fig. 8b) and finally into the resonant cavity. The focuser removes from the beam the molecules in the lower of the two energy states of interest, leaving in the beam entering the cavity only upper state molecules.

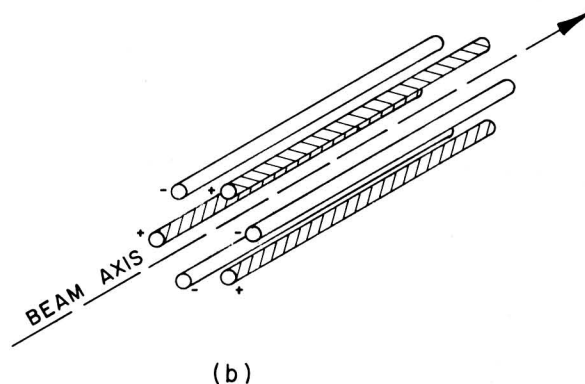
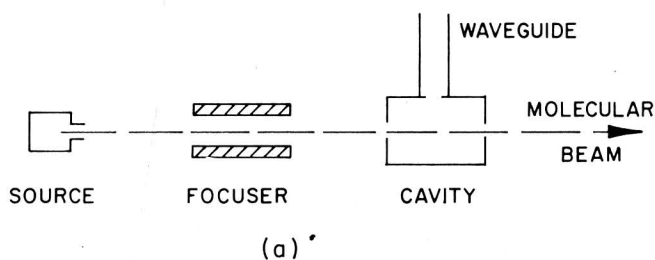


Fig. 8 - (a) Schematic diagram of a molecular beam Maser.  
(b) A perspective view of the focuser.

The action of the focuser can be understood by reference to Fig. 9. This shows how the energies of the internal states of the molecules vary in an electric field; it is seen that the energy of the upper state increases in a field, and the energy of the lower state decreases. Because of this (quadratic) Stark effect on the energy levels, a molecule placed in a region where the electric field has a gradient will experience a force; this will be toward the low field region for a molecule in the upper energy state, but toward the high field region for a lower state molecule. An inhomogeneous field region thus acts on the original beam of molecules so as to split it into two

<sup>19</sup> J. P. Gordon, "Hyperfine Structure in the Inversion Spectrum of  $N^4H_3$  by a New High-Resolution Microwave Spectrometer", *Phys. Rev.*, vol. 99, pp. 1253-1263, August 15, 1955; K. Shimoda, T. C. Wang and C. H. Townes, "Further Aspects of the Theory of the Maser", *Phys. Rev.*, vol. 102, pp. 1308-1321, June 1, 1956; J. C. Helmer, "Theory of a Molecular Oscillator," *Microwave Laboratory Report No. 311*, June 1956, Stanford University.

physically separated beams, a focused one consisting of upper-state molecules and a diffuse, deflected one of lower state molecules. The inhomogeneous field is produced in the focuser by a series of long, thin electrodes, parallel to the beam axis and surrounding it (see Fig. 8b). Alternate electrodes are charged to high and low potentials: this produces zero field along the axis and high fields near the electrodes. The upper state molecules in the beam thus experience a focusing force toward the beam axis, while the lower state ones are defocused out of the beam. Clearly, only molecules having this type of Stark effect can be used in the Maser.

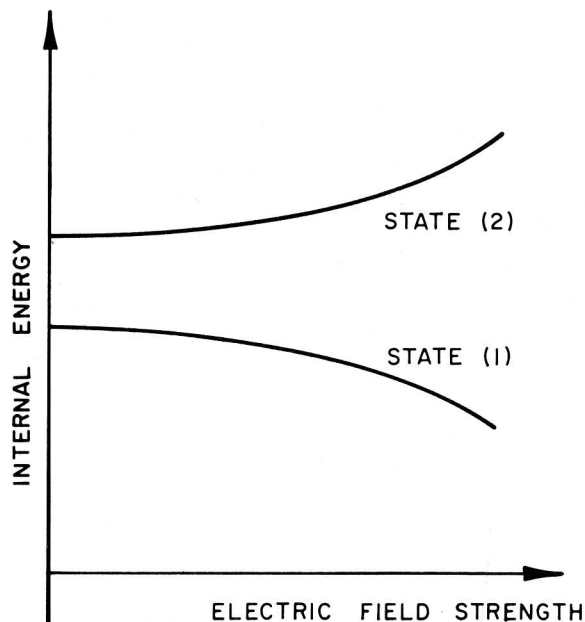


Fig. 9 - Stark effect in an ammonia molecule.

If the power emitted by the molecules exceeds the losses in the walls, the device can act as an amplifier. If the power emitted exceeds the sum of wall losses and the power coupled out of the cavity into the connecting waveguides, oscillations will build up until saturation effects make the molecularly-emitted power equal to all losses. The power emitted can be controlled by varying the beam density. Since it is possible to get beam densities high enough to sustain oscillations, the gain as an amplifier can be made essentially infinite, with, of course, a corresponding decrease of the amplification bandwidth to practically zero.

The bandwidth of the Maser is determined by a process not previously discussed. Since the beam is tenuous, gas collision broadening is absent, and if the  $TM_{010}$  mode in a cylindrical cavity is used, there is no axial variation in the microwave fields and Doppler effects are also missing. The coherent interaction time is then determined by the transit-time, i.e., the time it takes for

a molecule to travel the length of the cavity. The "molecular bandwidth" is of the order of<sup>20</sup>

$$(\text{Molecular bandwidth}) \approx \frac{1}{T_2} \approx \frac{v}{\ell},$$

where  $\ell$  is the cavity length and  $v$  the mean molecular velocity.

In a molecular-beam Maser, the internal energy emitted as microwave energy is acquired during the collisions of the molecules with the walls of the source chamber whereby they come into thermal equilibrium with this chamber. The kinetic energies of motion of the molecules arise in the same way. If the gas admitted to the source chamber is already at the temperature of the chamber, there is no further transfer of energy to the gas from the chamber.

When the Maser is acting as a linear amplifier, only a small fraction (a few percent) of the total internal molecular energy is transformed to microwave energy, and hence the Maser efficiency is low. Acting as an oscillator, some non-linearity of emission is inherent, and the efficiency can be somewhat higher. The kinetic energy of the molecules is not converted to microwave energy, but is lost when the "spent" gas is pumped away after traversing the amplifier cavity. If this is included in calculating the efficiency, the efficiency is low indeed, as the kinetic energy of a molecule leaving a source at room temperature is typically hundreds of times its total internal energy available for conversion to microwaves.

One gas suitable for use in a Maser is ammonia: here the "inversion" transitions provide suitable pairs of levels for focusing. The strongest set of levels has a transition frequency at 23.870 kmc (1.26 cm). Cavities roughly 10 cm long give a transit-time bandwidth of about 6 kc; the amplification bandwidth is somewhat smaller, depending on the amplifier gain. Assuming a loaded cavity  $Q_L = 5000$  and unloaded  $Q_0 = 10000$ , the saturation condition for linear amplification (Eq. (11) indicates that the incident signal power must be

$$P_{inc} < 10^{-10} \text{ watts.}$$

Another important property of the Maser is its noise figure. However, it is extremely difficult to measure noise figures as low as expected for such an amplifier, and no conclusive measurements have been made. The measurements made indicated a Maser noise figure of about one, i.e., zero db.

<sup>20</sup> A suitable average over the distribution of velocities must of course be taken, but this only introduces a numerical factor of order one.

As an oscillator, the Maser has the very high spectral purity to be expected of a very narrow band amplifier. (The molecular bandwidth is about 3 parts in  $10^7$  of the central frequency, giving an amplification bandwidth of only a few kilocycles.) Experimentally<sup>1</sup>, a spectral purity of about 4 parts in  $10^{12}$  has been obtained for a period of the order of one second. The power generated by the device when oscillating was estimated to be a few times  $10^{-10}$  watts.

The questions arise: what can be done to improve various operating characteristics, or alternatively, to what extent can performance in one respect be enhanced at the cost of worsened behavior in another characteristic? As an amplifier, the main characteristics desired are high gain, broad bandwidth, low noise figure, and high power-handling capabilities. As an oscillator, spectral purity and power are wanted. High gain in the Maser is easily assured. The amplification bandwidth can be increased if the transit time is reduced. This is most readily accomplished by shortening the cavity in the direction of beam travel. However, unless the beam geometry is altered, this reduces the number of molecules in the cavity at any one time and hence reduces the power emitted by the molecules. Unless the cavity losses are cut proportionately, the available gain is thereby reduced and the noise figure increased. One way to maintain a high number of molecules in a shortened cavity is to use multiple beams, but this introduces serious problems of pumping and obtaining a high cavity  $Q$ . Gain can also be traded for increased bandwidth by increasing the coupling of the cavity to the waveguide (reducing the loaded  $Q_L$ ). The bandwidth can be increased by either method without loss of gain if the beam flux can be increased. Oscillator power can also be increased by increasing the flux. Considerable effort is being made to improve gas sources to increase beam densities.

There are several other practical problems in connection with the Maser that are receiving attention. Improvement of focusing methods is one. Also, since molecules must pass from the source through the focuser and cavity without colliding with other molecules, a high vacuum is needed, and various improved pumping schemes are under consideration. With its high spectral purity and its frequency basically determined by molecular properties, the Maser should provide a good atomic frequency standard. However, the exact frequency of oscillation can be "pulled" slightly by the resonant cavity or by stray fields. Various methods of eliminating or allowing for such pulling effects are being studied. Finally, the question of the tunability of a Maser amplifier arises. As seen above, the energy separation of the two states, and hence the molecular transition frequency, can be altered by an electric field. A magnetic field can often have a similar result. However, problems of uniformity of tuning field (and degeneracy-splitting effects) make it practically impossible

to change the resonance frequency more than a megacycle by these methods; the molecular beam Maser is essentially untunable.

### B. Hot-Grid State Separator

Another type of molecular amplifier is the "hot-grid cell" devised by R. H. Dicke.<sup>21</sup> The way a gas is maintained in an emissive condition in this device can be seen with reference to Fig. 10. Figure 10a is a schematic cross-section of one configuration of such a device. The microwave structure consists of a plane parallel plate waveguide, the plates being labeled "Cold Wall" and "Hot Wall" for a reason that will shortly become clear. The microwave fields are assumed to be in the form of a wave propagating between these conducting plates and into the plane of the paper. Adjacent to the hot wall is a grid of fine wires parallel to the hot wall and each other and maintained at a high voltage with respect to the hot wall. This produces a region of intense electrostatic field around the wires and along the hot wall. In the following, it is assumed that the grid is completely transparent to gas molecules, to simplify the discussion. This clearly is only an approximation. However, by heating the grid structure itself, it becomes an "equivalent hot wall" and itself behaves as the actual hot wall. The region between the walls is filled with a gas, such as ammonia, that has a Stark effect as shown in Fig. 6, and is at a pressure such that the mean free path for gas-gas collisions is several times the distance between walls. Such collisions can thus be neglected. Figure 10b shows the distribution of electric field strength in the cell; Fig. 10c is a plot of internal energy of a gas molecule as a function of position in the cell for molecules in the upper and lower of the two energy levels of interest. It is seen that in the bulk of the cell, between the cold wall and grid, there is no electric field (other than the microwave field) and the two energy levels are separated by the usual amount,  $\Delta W = h\nu_0$ , where  $\nu_0$  is the frequency of the microwave field at resonance.

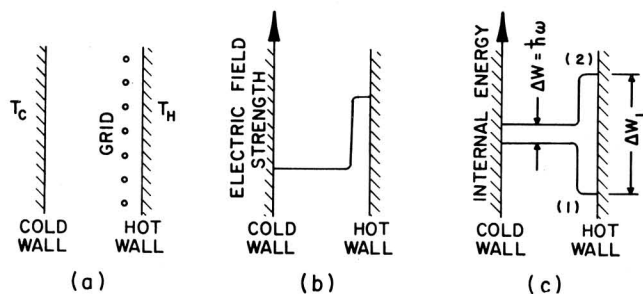


Fig. 10 - Temperature, electric field strength and internal energy as a function of position across a hot grid separation cell.

<sup>21</sup>R. H. Dicke, private communication.

Gas molecules that strike the cold wall become "thermalized" at its temperature  $T_c$ . This means that they leave the wall with velocities characteristic of a Maxwellian distribution at  $T_c$ , and with a distribution between the two internal energy levels given by Eq. (4), with  $T = T_c$ . Thus the class of molecules moving toward the right after striking the cold wall contains more molecules in the lower energy state than the upper, and has a net absorptive effect. As the molecules move toward the hot wall, those in the upper energy state see a repulsive barrier in the region of high electrostatic field and tend to be reflected back toward the cold wall. Molecules in the lower state are attracted into the potential energy well along the hot wall (Fig. 10c) and hence strike the hot wall (or hot-grid structure).

The height of the repulsive barrier seen by the upper state molecules depends on the strength of the electric field; however, with a Maxwellian distribution of velocities, some upper state molecules will possess sufficient kinetic energy to surmount the barrier and strike the hot wall, regardless of barrier height. The molecules that are reflected back to the cold wall form a second, smaller class of molecules; this class, composed as it is of upper state molecules only, is strongly emissive.

A third group of molecules consists of those leaving the hot wall and returning to the cold wall. These molecules leave the hot wall in equilibrium with it at its temperature  $T_H$ . However, the energy difference  $\Delta W_1$  between the two states in the strong field at the wall is much greater than  $\Delta W = h\nu_0$ , and so, by Eq. (4), many more molecules leave the hot wall in the lower energy state than in the upper. Now it is the lower state molecules that have to surmount a Stark field barrier to return to the cold wall, while the field accelerates the upper state molecules in their return journey. The net result is that this third group of molecules, containing both upper and lower state molecules, is absorptive, i.e., has a higher density of lower than of upper state molecules in it.

The net effect of these three groups of molecules depends on  $T_c$ ,  $T_H$  and the height of the electrostatic field barrier. If  $T_c = T_H$ , the gas in the field-free region between the "cold" wall and grid is in thermal equilibrium with the walls, and hence is absorptive, regardless of the high-field region. However, if the temperature of the cold wall is lowered,  $T_c < T_H$ , two effects occur. One is that the proportion of molecules in the lower state leaving the cold wall increases, by Eq. (4). This is a relatively unimportant effect. Lowering  $T_c$  has the more significant result that the kinetic energies of the molecules leaving the cold wall are reduced, and more of these slower molecules are reflected at the field barrier, increasing the number of molecules in the emissive, reflected class. Raising the hot wall temperature  $T_H$  has a similar result, for different reasons. By increasing  $T_H$ , more molecules leaving the hot wall are in the upper energy level, (from

Eq. (4)). There is also the result that the molecules returning from the hot wall are speeded up by raising  $T_H$ , and since this is an absorptive class of molecules, by thus decreasing their transit time to the cold wall, their density, and hence absorptive effect, is reduced for a constant molecular flux. The net result can be that, for suitable  $T_c$ ,  $T_H$  and field barrier height, the gas is maintained in an emissive condition in the main part of the cell.

An exact analysis of such a grid cell is exceedingly difficult, as it depends on suitable averages to determine such parameters as the "effective field barrier height", a spatial average over the inhomogeneous field produced by the grid structure. However, estimates indicate that the "excess population",  $(N_2 - N_1)$ , can be of the order of one percent of the total number of molecules for temperatures of the order  $T_c \approx -100^\circ\text{C}$ .,  $T_H \approx 200^\circ\text{C}$ ., and fields produced by appropriate grid structures at 15-20 kv voltages. This corresponds to a gain coefficient (Eq. (13)) of the order of  $\alpha \approx 10^{-3}\text{cm}^{-1}$ . This is too small to make a non-resonant waveguide amplifier practical: an amplifier many meters long would be required to produce useful gain. It is, nevertheless, large enough to make a low-noise amplifier possible using a resonant cavity type of microwave structure; as seen above, with a cavity amplifier, the gain can be made arbitrarily large, (with an unavoidable loss of bandwidth).

It might be expected that transit time effects across the cell would determine the amplification bandwidth. This, however, is not the case. For satisfactory operation of the cell, a rectangular cell cross-section is desirable. To make a very low loss cavity with this geometry, one several wavelengths long is required. In this case, Doppler effects can not be neglected, and indeed provide the dominant broadening mechanism. For ammonia as the active gas, the Doppler-determined molecular line breadth is of the order of 50 kc, about an order of magnitude larger than for a beam-type Maser. This greater bandwidth is accomplished without loss of gain, despite the small fractional upper state enrichment, by the much higher molecular densities achieved with the hot-grid cell compared with the molecular beam Maser.

The Maser, with its narrower bandwidth, is expected to be much more stable as an oscillator than the hot-grid cell. Thus, for frequency standard applications the beam type of device is to be preferred. On the other hand, the hot-grid cell can be operated as a sealed off device without the continual supply of gas and its subsequent removal as in a beam amplifier.

The efficiency of a hot-grid cell is low. In addition to the loss taken to preserve linear operation, the thermal losses as the molecules travel from hot wall to cold are enormous relative to the microwave energy conversion. (Here again, as in the beam Maser, the internal energy comes from the thermal energy of the cell walls.)



### C. Pulse Inversion

One of the methods of achieving an emissive state discussed above is essentially a continuous process, i.e., the hot-grid cell. The other, molecular-beam separation of states, while separating the exciting region from the utilization region, nonetheless uses a continuous flow of gas to achieve effectively cw operation. There are, however, other means of exciting a molecular system that are distinctly pulse-operation approaches. "Pulse inversion of states" is one of these. From Eq. (6) it follows that if a system is exposed to a pulse of microwave power on resonance ( $\nu = \nu_0$ ) of such strength and duration that

$$\frac{pET}{h} = \frac{1}{2}, \quad (24)$$

molecules originally in the lower state will be raised to the upper state and vice versa; i.e., the state populations will be *inverted*. Thus, such a pulse transforms an absorptive system into an emissive one. The pulse duration must be short compared to the relaxation times, or complete inversion is not achieved. This is not a serious limitation, however, as with readily available powers, pulses of under a microsecond duration satisfy Eq. (24). Two conditions are critical in this method of obtaining an emissive state: (a), if the pulse frequency is off resonance, complete inversion will not be obtained (see Eq. (6)), and (b), the product of pulse strength and duration must be accurately adjusted.

An amplifier can be made by putting a molecular system in a suitable microwave structure such as a resonant cavity and exciting it with an inverting pulse. For a period of time given by the relaxation processes, the cavity with its emissive loading will amplify microwave signals incident upon it in a frequency bandwidth corresponding to the gain bandwidth of the amplifier.

This excitation method offers the possibility of relatively high efficiency, on a molecular basis, if a system with  $T_1 \gg T_2$  is used, and some time-dependence of the amplifier gain is allowed. Apart from resistive losses in the microwave structure, much of the energy supplied in the excitation pulse can be re-extracted in the amplification period. However, if the power requirements of the electronic devices needed to generate and control the inverting pulses are included in the calculation, even this excitation scheme results in low efficiency.

Such a device has obvious faults as an amplifier. It amplifies only for a fraction of the time, and is non-amplifying in the excitation and the "thermalization" period in which equilibrium is again attained before the

next inverting pulse. The gain is therefore periodically varying. If the device operates at room temperature, the noise figure cannot be better than 3 db, from Eq. (23). This can be improved by going to low operating temperatures; at liquid helium temperatures, the minimum noise figure is under 0.1 db. A serious fault of this method of achieving state-population inversion is that it depends on a critical adjustment of frequency and pulse strength and duration. Means of overcoming these difficulties will be discussed in connection with a second pulsed method of obtaining an emissive state.

### D. Inversion by Adiabatic Fast Passage

Bloch<sup>14</sup> has shown that spin systems in a static magnetic field can be inverted by what is called *adiabatic fast passage*. His results can be generalized<sup>22</sup> to show that state populations in an arbitrary two-level system can be inverted by a similar technique. In adiabatic fast passages, the molecular system is subjected to a strong microwave field of amplitude  $E$  and variable frequency. The frequency of this field starts far off resonance and is slowly swept through the resonant frequency until it is far off resonance on the other side. When this has been done, the state populations are inverted. Three conditions must be met for this to occur:

(a) The passage must be adiabatic; that is, the frequency must be changed slowly compared to the internal motions of the molecule in response to the driving field  $E$ . This condition can be expressed as

$$\frac{d\nu}{dt} \ll \frac{pE}{h}.$$

(b) The passage must be fast compared to the relaxation time; the time  $\tau_S$  required to sweep the frequency from one side of resonance to the other must be short compared to the relaxation time  $\tau_r$  of the system.

$$\tau_S \ll \tau_r.$$

(c) The driving field  $E$  must be larger than the maximum radiation field of the system. During the passage through resonance, the molecular system develops an oscillating dipole moment; the maximum radiation field of this moment must be smaller than the driving field or population inversion can not be achieved.

<sup>22</sup>S. Bloom, private communication.

A physical explanation can be given for each of these requirements. In an adiabatic fast passage, the molecular system goes through a series of quasi-stationary states. If the sweep rate is too large, the system cannot follow the changes adiabatically, and non-stationary states, such as are responsible for pulse inversion, are induced. The second condition merely assures that the inversion is completed before the competing relaxation processes can restore the system to thermal equilibrium. The third condition arises because the radiation field and driving field become out of phase as they approach each other in magnitude, and at equality of magnitudes, they just cancel each other in their effects.

Two other points of importance should be mentioned. One is that it does not matter in which direction the frequency sweep traverses the resonance: the initial frequency can be either above or below the resonant frequency. The second is that if the resonant frequency of the molecular system can be altered, by the application or change of an applied electric or magnetic field for example, the inversion can be achieved by keeping the frequency of the applied microwave field fixed and *sweeping the resonant frequency* from one side of the applied frequency to the other.

Adiabatic fast passage has two major advantages over pulse inversion as a method of achieving an emissive state: it is not necessary to control the frequency of the microwave exciter source accurately, and the exact duration and time dependence of the frequency sweep are similarly uncritical. The other difficulties of pulse inversion enumerated above are also met in adiabatic fast passage. However, as mentioned earlier, most if not all are susceptible to amelioration. Before discussing this, the characteristics desirable in a molecular system excited by adiabatic fast passage will be considered.

From Eq. (13), the gain coefficient  $a$  increases with the number of "excess" molecules  $N$  and the dipole moment  $p$ , and decreases with increasing molecular bandwidth as

$$a \sim \frac{p^2 N}{(\text{Bandwidth})}$$

Since amplification bandwidth is at a premium, it is clear that systems with a large "excess" population are desirable: if state population inversion is to be used, a large excess at thermal equilibrium is wanted. From Eq. (5a),  $N_1 - N_2 = N_{tot} \tanh(h\nu/2kT)$ , a large excess can be obtained in two ways, by increasing the molecular density or by going to lower temperatures.

Low temperatures are also desirable from a noise figure point of view, as is seen by considering Eq. (23).

Neglecting guide losses,

$$F_{min} = 1 + \left( \frac{N_2}{N_2 - N_1} \right) \frac{h\nu}{P_{No}}$$

Starting from a state of thermal equilibrium at a temperature of the molecular system  $T_{molec}$ , after state inversion

$$\frac{N_2}{N_1} = \exp \left( + \frac{h\nu}{kT_{molec}} \right)$$

and

$$\frac{N_2}{N_2 - N_1} \approx + \frac{kT_{molec}}{h\nu}$$

The noise figure is referred to room temperature  $T_0$ ,

$$P_{No} \approx kT_0$$

and

$$F_{min} = 1 + \frac{T_{molec}}{T_0} \quad (25)$$

Thus noise figures of under 3 db can only be achieved by lowering the temperature of the molecular system: at dry ice temperatures,  $T_{molec} = 194^\circ\text{K}$ ,  $F_{min} = 2.3$  db, at liquid nitrogen temperatures,  $T_{molec} = 77^\circ\text{K}$ ,  $F_{min} = 1.1$  db, while at liquid helium temperature,  $T_{molec} = 4^\circ\text{K}$ ,  $F_{min} = 0.06$  db.

The desirability of both low temperatures and high densities points toward use of a solid molecular system. However,  $a \sim p^2$  argues for a gas, where electric dipole transitions with  $p \sim 10^{-18}$  are available, and against a solid, where only paramagnetic resonance for which  $p \sim 10^{-20}$  appears to provide sufficiently long relaxation times. Relaxation times in a gas of useful density are short, however, making the sweep technique of adiabatic fast passage very difficult to apply. Turning then to a solid (or liquid), the problem of finding a molecular system with a useably long relaxation time arises. Fortunately, systems are known with spin-lattice relaxation times of the order of many seconds.<sup>23</sup> These are systems of paramagnetic electrons localized on donor atoms in a silicon lattice. The donor atoms whose relaxation times

<sup>23</sup> G. Feher and R. C. Fletcher, "Relaxation Effects in Donor Spin Resonance Experiments in Silicon", *Bul. Am. Phys. Soc.*, vol. 1, p. 125, March 15, 1956 (Pittsburgh Meeting).

have been measured include Group V elements (P, As, Sb) and lithium. The relaxation times vary with temperature and donor concentration, but for concentrations less than  $10^{17} - 10^{18}$  donors per cubic centimeter and at liquid helium temperatures,  $T_1$  is of the order of a minute. Thus suitably doped silicon at liquid helium temperatures presents a high-density, long-relaxation-time material suitable for making a low-noise amplifier<sup>24</sup> excited by adiabatic fast passage.

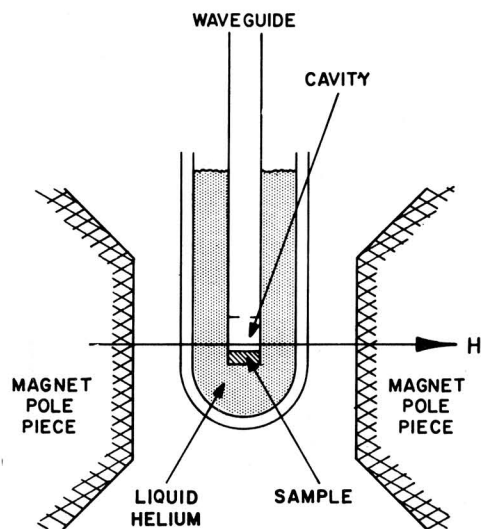


Fig. 11 - Low-temperature paramagnetic amplifier.

A possible amplifier using adiabatic fast passage excitation might consist of a doped-silicon sample in a microwave cavity in a helium cryostat located between the poles of an electromagnet, (Fig. 11). The time variation of the (dc) magnetic field  $H$  for such an amplifier is shown in Fig. 12. At point A, the sample is in thermal equilibrium with its surroundings in a magnetic field  $H_A$ . From A to B, the magnetic field is swept through  $H_R$ , which is the resonant field at the exciter microwave field frequency. This adiabatic fast passage inverts the spin state populations, leaving the sample in an emissive condition. From B to C, the field is kept constant at  $H_B$ , and the device acts as an amplifier of microwaves at the frequency

$$\nu = \gamma H_B = 2.8 H_B mc.$$

At C, the field is abruptly returned to  $H_A$ , reaching  $H_A$  at D. Amplification at the frequency  $\nu$  ceases, and the

system is allowed to come to thermal equilibrium with its surroundings in the field  $H_A$ . Thermalized again at A', the cycle is repeated. This cycle produces a pulsed amplifier, with an amplification period from B to C and a dead-time, during which it is re-excited, from C to B'.

At first thought, it would seem that the dead-time C-B' would greatly exceed the active time B-C, since a time D-A' long compared to  $T_1$  is required for the sample to reach thermal equilibrium. Fortunately, however, with a doped-silicon sample something can be done to shorten D-A' drastically. The long relaxation time ( $\sim 1$  minute) of this material at liquid helium temperatures is associated with the fact that the paramagnetic electrons are bound in the Coulomb-type potentials surrounding the donor atoms and that there are no free (conduction) electrons in the sample. If the sample (at liquid helium temperature) is illuminated with visible light, free carriers are released and  $T_1$  is reduced to the order of a microsecond. A flash of light can thus shorten the required time for thermalization D-A' to a few microseconds. With an adiabatic sweep time A-B of a few milliseconds and an amplification time B-C of several seconds, it is seen that a nearly continuously amplifying device can be made. (It should be mentioned that by exciting the sample externally to the amplifier cavity, and providing a continuous "flow" of excited material through the amplifier, a truly steady state, or continuous amplifier can be obtained.)

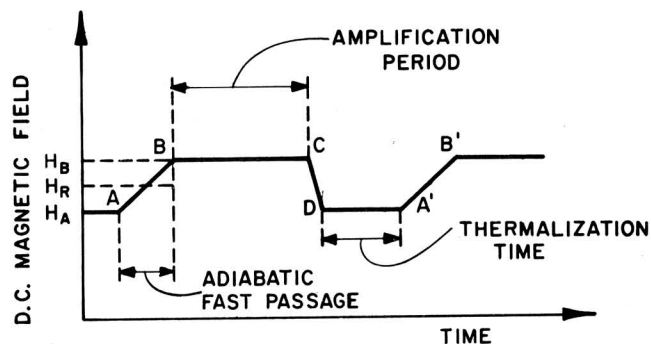


Fig. 12 - Magnetic field versus time for a paramagnetic amplifier excited by adiabatic fast passage.  $H_b$  is the field during the amplification period,  $H_r$  the field at which the molecules are resonant at the exciter field frequency, and  $H_a$  field at which thermalization occurs.

The power available from the molecular system after excitation is given by

$$P_{\text{emission}} = \frac{4\pi^2 N p^2 \nu T_2 H_r^2}{b},$$

where  $N$  is the excess number of spins in the upper state.

<sup>24</sup> J. Combrisson, A. Honig et C. H. Townes, "Utilisation de la resonance de spins électroniques pour realiser un oscillateur ou un amplificateur en hyperfréquences", *Compt. Rend.*, vol. 242, pp. 2451-2453, May 14, 1956.

The spectral line width is about

$$(\text{Bandwidth}) \approx \frac{1}{\pi T_2}.$$

Making the resistive losses in the cavity less than the emitted power by using high spin densities, using samples with sufficiently long  $T_2$ , and using a high- $Q$  cavity, a high-gain cavity amplifier can be obtained.

The molecular bandwidth associated with the doped-silicon samples discussed above is several megacycles, indicating a  $T_2$  of less than a microsecond. This is radically lower than  $T_1 \approx 60$  seconds. The difference is caused by magnetic interactions between the paramagnetic spins and between these spins and other magnetic dipoles in the sample (nuclear moments). These interactions dephase the electron spin-radiation field interaction, and hence broaden the resonance, but do not provide a means of exchanging energy with the crystalline lattice, and hence do not shorten  $T_1$ . By removing some of the dephasing nuclear moments and replacing them with non-magnetic isotopes,  $T_2$  can be increased and hence the molecular emission power increased, at, of course, a sacrifice of some amplification bandwidth.

The energy input in adiabatic fast passage comes from two sources: the high-level microwave exciter field, and, (possibly), the energy associated with the magnetic moment of the system if the applied field is varied. With available cavity  $Q$ 's, the losses from the exciter field are far greater than the microwave energy obtained in amplification, and so the efficiency of this system is low.

### E. Multi-Level Excitation Methods

The methods of achieving an emissive state discussed thus far have dealt with molecular systems where only two energy levels were significant.<sup>25</sup> There are other ways of obtaining an emissive state if one considers multi-level schemes and admits the possibility of one or more exciter frequencies different from the amplification frequency. Several possibilities for three-state systems have been discussed by Basov and Prokhorov.<sup>26</sup> One basic approach with a three-state system can be seen by reference to Fig. 13. In one embodiment (Fig. 13a), the upper pair of states (2) and (3) are separated by the microwave frequency desired to be amplified,  $\nu_{23} = \nu_{sig}$ .

<sup>25</sup> In these two-level systems, other levels are of practical importance in determining the fraction of the total molecules in the system in the two levels of interest.

<sup>26</sup> N. G. Basov and A. M. Prokhorov, "Possible Methods of Obtaining Active Molecules for a Molecular Oscillator", *J. Exper. Theoret. Phys. USSR*, vol. 28, pp. 249-250, February, 1955.

Energy states (1) and (3) are also coupled by a radiation field, of frequency  $\nu_{13} = \nu_{ex}$ . At thermal equilibrium, there are more molecules  $N_{1eq}$  in state (1) than in either state (2),  $N_{2eq}$  or state (3),  $N_{3eq}$ ; in fact,

$$N_{1eq} > N_{2eq} > N_{3eq}.$$

If the resonance at  $\nu_{ex} = \nu_{13}$  is saturated, however, this situation is altered. Here "saturated" means that the radiation field at frequency  $\nu_{13}$  is so large that the effects of induced transitions completely over-ride relaxation effects and the two states become equally populated. Saturating the transition at  $\nu_{13}$  results in increasing the population  $N_3$  of state (3). If this results in  $N_3 > N_2$ , a steady state emissive condition is obtained. It must be noted that relaxation effects, despite the strong rf field at  $\nu_{13}$ , may be very important in the final effective state populations attained. For example, if the relaxation mechanisms bringing the state populations  $N_3$  and  $N_2$  into thermal equilibrium are very weak, while those thermalizing  $N_1$  and  $N_2$  are strong, as state (1) is depopulated by the radiation, the relaxation mechanisms will transfer molecules from state (2) to state (1), in an attempt to maintain the equilibrium  $N_2/N_1$  ratio. This will make the effective  $N_2$  less than that corresponding to a condition of thermal equilibrium for the whole sample. It is clear that with a complicated system of levels and relaxation effects, many variations on this theme are possible. An obvious one is shown in Fig. 13b: here the  $\nu_{13}$  transition is again saturated, but a fast relaxation between states (3) and (2) together with a weak relaxation mechanism between (1) and (2) now makes  $N_2 > N_1$  and amplification occurs at a frequency  $\nu_{sig} = \nu_{12}$ .

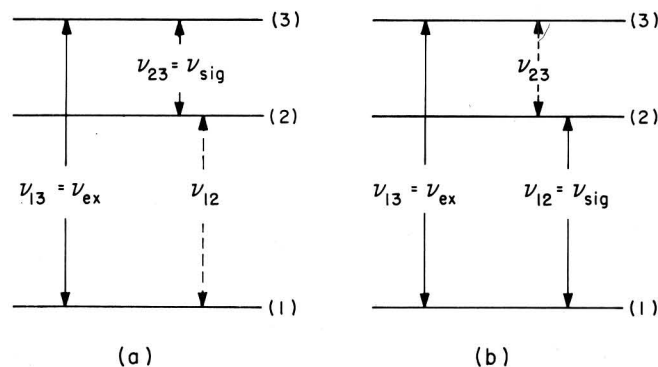


Fig. 13 - Energy level diagram illustrating multi-level excitation methods.

This general method of achieving an emissive molecular system can have the exceedingly desirable feature of combining the high molecular densities availa-

ble in a solid with the continuous excitation of the gas devices discussed by using a solid with appropriate energy levels and relaxation times. Some practical problems are posed by this excitation method, however. Since excitation is a continuous process, the same cavity must be used for both excitation and amplification. This means a cavity simultaneously operating in two modes, at two frequencies. Furthermore, the modes must be chosen so that, insofar as possible, regions of strong field for the excitation processes and regions of strong interaction for the amplification process coincide. This requirement cannot be met completely, of course, because of cavity mode orthogonality. However, with small sample sizes, this is a minor problem. If the amplifier operates at liquid helium temperatures, the heating effects of the saturating exciter field must also be considered. As in excitation by adiabatic fast passage, the presence of a strong exciter field with its relatively high losses makes multi-level excitation methods have low efficiency.

Multi-level methods of excitation open up another possibility of achieving low-noise amplification without resorting to low temperatures. Neglecting guide losses, the noise figure can be written, Eq. (25),

$$F = 1 + \frac{T_{molec}}{T_0},$$

where  $T_{molec}$  is the "internal temperature" of the molecular system, defined by Eq. (2). With excitation methods that exchange, or invert, state populations, a  $T_{molec} < T_0$  can only be achieved by physically cooling the molecular system, ( $T_0$  is defined to be room temperature). With the multi-level excitation scheme of Fig. 13, however, if the spin-lattice relaxation time  $T_{12}$  coupling states (1) and (2) is very much shorter than the relaxation time  $T_{23}$  coupling states (2) and (3), the internal temperature for the amplifier resonance between (2) and (3) is given by:

$$T_{molec} = \frac{\nu_{23}}{\nu_{12}} \times (\text{Actual amplifier temperature})$$

If  $\nu_{23}$  is sufficiently below  $\nu_{12}$ , the actual amplifier temperature can be room temperature and low-noise figures can still be obtained.

A major problem associated with this multi-level excitation method is in finding a suitable molecular system. The requirements are rather stringent: (a) the system must have three levels as shown in Fig. 13, with separations such that  $\nu_{ex}$  occurs at a frequency where oscillators of reasonable power exist, and such that  $\nu_{sig}$  is a desirable amplification frequency; (b), the selection rules must permit the transitions at  $\nu_{13}$  and  $\nu_{23}$  to be induced

by radiation; (c), the relaxation time  $T_{13}$  must be long enough to permit saturation of the excitation resonance; (d), the relaxation time  $T_{23}$  must be considerably greater than  $T_{12}$ ; (e), molecular densities must be high enough so that molecularly emitted power exceeds the losses at signal frequency. Requirement (d) can be expressed mathematically by

$$T_{23} > T_{12} \frac{N_{2eq} - N_{3eq}}{N_{2eq} + N_{3eq}} \frac{N_{1eq} + N_{2eq}}{N_{1eq} - N_{2eq}}$$

where  $N_{ieq}$  is the population of the  $i^{th}$  level under conditions of thermal equilibrium (with no microwave fields present).

Fulfilling all five above requirements can only be done using very special systems. Such systems can be found in the energy level spectra of certain paramagnetic transition metals, using suitable compounds to achieve desired crystalline field splittings of otherwise degenerate energy levels. Work on an amplifier using multi-level excitation is being undertaken at Harvard University<sup>27</sup> and elsewhere.

#### F. Optical Pumping

Still another way to achieve an emissive state utilizing several energy levels is known as "optical pumping".<sup>28</sup> In "optical pumping", the system is illuminated with suitably polarized light of a wavelength corresponding to an optical transition of the molecules. The absorption of this polarized light, and subsequent spontaneous emission of unpolarized light can result in a rearrangement of molecules among a group of states such that those in two states connected by a microwave transition are in an emissive condition. To see this in more detail, consider an atom (molecule) with the (partial) energy level system shown in Fig. 14. There are two sets of energy levels of interest: the upper set consists of five degenerate levels and is separated from the lower set of three degenerate levels by an "optical transition" ( $\nu = 10^{14}$  to  $10^{15}$  sec.<sup>-1</sup>). The levels are designated by the quantum

<sup>27</sup> N. Bloembergen, "Proposal for a New Type Solid State Maser", *Phys. Rev.*, vol. 104, pp. 324-327, October 15, 1956.

<sup>28</sup> A. Kastler, "Quelques Suggestions Concernent la Production Optique et al Detection Optique d'une Inegalite de Population des Niveaux de Quantification Spatiale des Atoms", *J. Phys. Rad.*, vol. 11, pp. 255-265, June 1950; J. Brossel, A. Kastler et J. Winter, "Creation Optique d'une Inegalite de Population Entre les Sous-Niveaux Zeeman de l'Etat Fondamental des Atoms", *J. Phys. Rad.* 13, p. 668, Dec. 1952, W. B. Hawkins and R. H. Dicke, "The Polarization of Sodium Atoms", *Phys. Rev.*, vol. 91, pp. 1008-1009, August 15, 1953.



numbers  $F$  and  $M_F$ .  $F$  is the total angular momentum of the atom, in units of  $h/2\pi$ , about the  $Z$ -axis, and  $M_F$  is the component of  $F$  along the  $Z$ -axis.

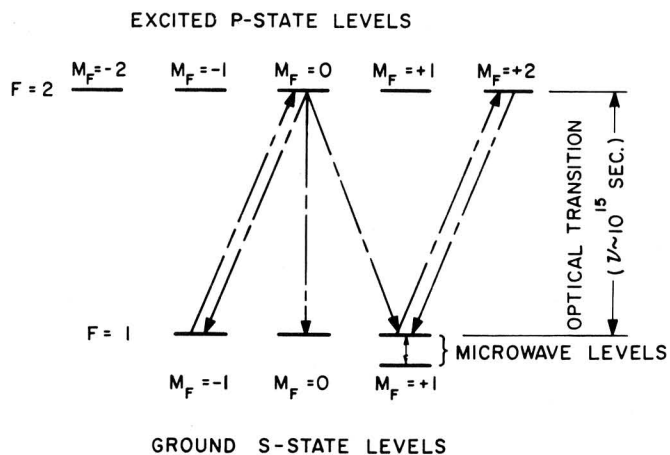


Fig. 14 - Schematic energy level diagram showing optical transitions as used in "optical pumping".  $M_F$  is the component of total angular momentum  $F$  along the axis of the system.

Consider what happens to an atom that absorbs a photon from a beam of circularly polarized light traveling in the  $Z$ -direction. Such a photon carries a  $Z$ -component of angular momentum of one unit and one unit of total angular momentum. Assume the sense of polarization is such that the photon has an effective  $M_z = +1$ . Then the selection rule for absorption is  $\Delta M_F = +1$ , and an atom originally in the  $F = 1, M_F = -1$  state goes into the  $F = 2, M_F = 0$  state upon photon absorption. Atoms in the upper set of levels are highly excited, however, and reemit a photon spontaneously in about  $10^{-8}$  seconds. This photon is generally unpolarized, as the selection rule for spontaneous emission is  $\Delta M_F = +1$  or  $0$ . This is indicated for the  $F = 2, M_F = 0$  state on Fig. 14. It is seen that after a complete cycle of absorption and reemission, an atom originally in the  $F = 1, M_F = -1$  state can be in any of the three  $F = 1$  states. An atom that was initially in the  $F = 1, M_F = +1$  state, however, must remain in the same state after a cycle, as the only transition possible in re-emission is the  $\Delta M_F = -1$  one.

Illumination of the system with polarized light can result in an effective depopulation of some levels ( $F = 1, M_F = -1$  in the case above) and an increase in population of others ( $F = 1, M_F = +1$  above). If a state that is increased in population is also coupled by a microwave transition to a lower state (as shown in Fig. 14), an emissive condition may be maintained with respect to these two levels. Such a gas of atoms could be used in a suitable microwave structure as an amplifying or oscillating medium.

There are several practical difficulties besetting the utilization of this method for obtaining a molecular system in an emissive condition. First, a molecule or

atom having a suitable energy level scheme must be found. The alkali metal vapors and atomic hydrogen fulfill this requirement; the optical transition is between the  $^2S_{1/2}$  atomic ground state of the atoms and the first excited  $P$ -state, while the hyperfine structure of the ground state provides the microwave transition. Vapor pressures, which determine available gas densities, and, in the case of atomic hydrogen, recombination processes, must also be considered. If the optical transition is in either the near infrared or the ultraviolet, polarization difficulties may arise.

In the above description of the "optical pumping" process, several simplifying assumptions were made. One was that the absorption process could be considered to go between an initial state and one final state. The upper optical levels are very broad, however, and the possibility exists of two such states, to both of which the selection rules permit transitions, "overlapping". In this case, complex "interference" effects occur; their result is that the excited atom "remembers" the angular momentum absorbed and tends to reemit it again, thus leaving no net "pumping" effect. It was further implicitly assumed that only one of the two microwave-coupled levels was optically coupled to the upper optical levels. Because optical lines are so broad, this can not be achieved, and the populations of both of the microwave levels may be altered by "optical pumping". It can be shown, however, that in favorable cases both these possible sources of difficulty do not prevent an emissive state from being attained.

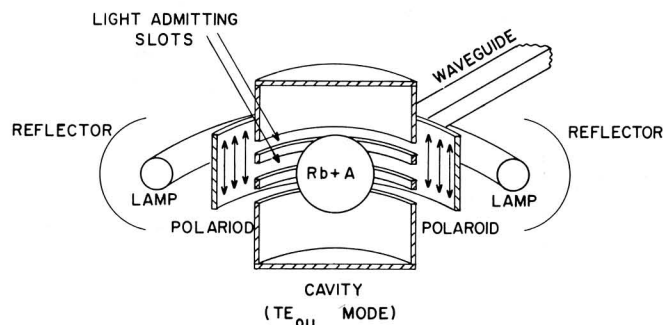


Fig. 15 - "Optically pumped" amplifier.

A sketch of one practical way in which an "optically pumped" amplifier might be achieved is shown in Fig. 15. The molecular system consists of rubidium vapor at a pressure of roughly  $10^{-6}$  mm Hg. The microwave transition is between the hyperfine levels of the ground state, and occurs at 6834.68 mc. The optical transition is in the near infrared at about  $7900 \text{ \AA}$ . This can easily be linearly polarized using Polaroid sheets. The rubidium vapor is contained in a small glass bulb at the center of the microwave cavity. Argon at a pressure of about one mm Hg is also in the bulb. This increases the diffusion time of the rubidium vapor to the walls of the bulb, and effectively



eliminates Doppler effects.<sup>29</sup> The cavity is cylindrical and resonant in the  $TE_{0,11}$  mode. The light, polarized along the cavity axis, is incident on the vapor through circular slots cut in the walls of the cavity. This can be done without greatly affecting the  $Q$  of the desired resonant mode. The effect of "optical pumping" on the population of the various hyperfine energy levels is shown in Fig. 16. At thermal equilibrium, the states are populated as shown on the upper series of energy levels. After each atom has absorbed and re-emitted an optical photon, the distribution is as shown on the lower series of levels. It is clear that for the three  $\Delta M_F = 0$  transitions, the system after "pumping" is highly emissive, and in fact corresponds to the very low negative internal temperature  $T_{molec} = 0.12^\circ\text{K}$ .

	$M_F = -2$	$-1$	$0$	$+1$	$+2$	
$F = 2$	<u>.999</u>	<u>.999</u>	<u>.999</u>	<u>.999</u>	<u>.999</u>	$\downarrow$ 6834 MC $\downarrow$
$F = 1$		<u>1.000</u>	<u>1.000</u>	<u>1.000</u>		
	RELATIVE STATE POPULATIONS BEFORE					
	PHOTON ABSORPTION					
$F = 2$	<u>.706</u>	<u>1.147</u>	<u>1.294</u>	<u>1.147</u>	<u>.706</u>	$\downarrow$ 6834 MC $\downarrow$
$F = 1$		<u>.952</u>	<u>1.098</u>	<u>.952</u>		
	STATE POPULATIONS AFTER EACH ATOM HAS					
	ABSORBED AND RE-EMITTED ONE OPTICAL PHOTON					
	(SAME NORMALIZATION AS ABOVE)					

Fig. 16 - Effect of "optical pumping" on the state populations of the magnetic sub-states of the hyperfine levels of the ground S-state of rubidium vapor.  $F$  is the total angular momentum of an atom and  $M_F$  its component along the axis of the system.

The major weakness of amplifiers based on this excitation method is a quantitative one. It seems neces-

sary to go to a gaseous system to find a molecular energy level scheme that is suitable. Furthermore, the density of the active gas must be relatively low, as indicated above, or "light trapping" occurs; that is, the optical photon re-emitted by one excited atom is reabsorbed by another before it can "escape" from the gas. Since the re-emitted photon is unpolarized, its reabsorption tends to "unpump" the atom absorbing it. Thus the total "excess population"  $N$  is very low. Also, at least in the molecular systems listed above, the microwave transition is a magnetic dipole one, with the accompanying low dipole moment  $p$ .

Because of these factors, to get amplification it is necessary to make the bandwidth extremely small. For this reason, optically pumped amplifiers may be limited to applications where this is an advantage: high spectral purity oscillators and frequency standards. A frequency standard or "atomic clock" using optically pumped rubidium vapor is under study at Princeton University.<sup>30</sup> The expected molecular bandwidth of this rubidium amplifier, with its utilization of a "buffer gas" to eliminate Doppler effects, is of the order of 100 cps. Since the amplification bandwidth, or noise-induced frequency modulation as an oscillator should be much less than this, a very high frequency stability should be achieved.

The calculation of an "oscillator parameter  $L$ " (see Section III.C.) for this device is difficult, as several unknown factors enter. However, an estimate indicates that a loaded cavity  $Q$  of about 60,000 is required to sustain oscillations, (i.e., for  $L = 1$ ). With the glass bulb in the cavity and the slots for the admission of the polarized light, this may be an unattainable  $Q$ . Even if it ultimately so proves, however, the device will provide an extremely sharp resonance that can be used for frequency control purposes.

The efficiency of an optically-pumped amplifier is very low. Nearly all of the (relatively) huge amount of energy supplied in the optical frequency range is lost, either in optical reradiation or in resistive losses to heat in the cavity.

## V. Discussion

The foregoing material gives some idea of the wide variety of devices and systems covered by the common title of "molecular amplifier". While it is believed that the most promising amplifier schemes now proposed or

being worked on have been included in this discussion, it is also quite certain that this listing is not a final, definitive one. The wide range of approaches to emissive states indicated have all been invented or developed with-

<sup>29</sup> R. H. Dicke, "The Effect of Collisions upon the Doppler Width of Spectral Lines", *Phys. Rev.*, Vol. 89, pp. 472-473, January 15, 1953.

<sup>30</sup> I am indebted to Dr. T. R. Carver of Princeton University for permission to quote the results of calculations on this device that he has made. The numerical example given in the text is based on his work.

in the past few years, and it seems highly unlikely that the field is already exhausted of novel solutions to its problems.

This diversity has in some respects precluded a general discussion of molecular amplifiers and oscillators, and necessitated separate descriptions for each of the excitation methods and molecular systems. The basic properties of all molecular amplifiers are quite similar, however. The weakness of the individual molecular interactions in the microwave region, of the order of  $10^{-5}$  to  $10^{-4}$  electron volts per molecule, argues strongly for the use of a resonant microwave structure for the region of interaction between molecules and radiation. With such a structure, which includes built-in positive feedback, gain is of itself no problem: by increasing feedback, i.e., cavity  $Q$ , any desired gain can be obtained. The problem of power losses in the microwave structure, on the other hand, is a real one. Nearly perfect loss-free structures are needed so that the weak molecular power exceeds losses by a sufficient margin to permit low-noise operation.

There are two main sources of noise in a molecular amplifier, noise caused by spontaneous incoherent emission from the excited molecules, and noise from emission induced by thermal radiation from the microwave structure.<sup>31</sup> The latter can often be reduced by cooling the microwave structure. Despite these noise sources, noise figures of under 1 db can be achieved, and in many communications and radar systems where the signal source is such that the background noise entering the amplifier is well below thermal noise at room temperature, this indicates a tremendous increase in sensitivity over conventional microwave amplifiers with noise figures in the range 5-15 db.

Low-noise figure is directly related to the spectral purity when the amplifier is operated as an oscillator. It was seen that the heretofore unattainable short-term frequency stability of a few parts in  $10^{12}$  can be achieved with the molecular beam Maser, thus opening up new possibilities for the design of super-stable frequency standards based on atomic processes. These provide a standard of frequency at any place on the earth independent of astronomical observations, radio-transmitted standard frequency signals, etc.

The power handling capabilities of molecular amplifiers have been seen to be low. In some applications, this is a definite disadvantage; for example, in military radar such an amplifier could easily be saturated by a jamming signal. In other applications, however, the low power handling ability of molecular amplifiers provides no serious limitation to their use.

A major problem of molecular amplification, in addition to that of reduction of losses in the microwave structure, is that of bandwidth, or, more exactly, gain-bandwidth. As seen above, gain can always be traded for bandwidth, by using an inhomogeneous Stark or Zeeman field to broaden the resonance, by increasing molecular density and hence shortening relaxation times, or by increasing the microwave coupling to the interaction cavity. However, when the molecular emission power is spread over a broad bandwidth, the gain and noise figure worsen. Achievement of a high total available molecular power therefore is of great importance. For gaseous molecular systems, molecular densities are low and bandwidths of a few kilocycles to a few tens of kilocycles are available. With solid-state devices, bandwidths of megacycles should be obtainable.

In addition to gain, noise figure and bandwidth, frequency coverage is of importance. If the amplification frequency is determined by internal molecular properties, such as in ammonia and possibly in some solid state systems, the frequency is essentially fixed. In some applications, such as a frequency standard, this is desirable, or at least not objectionable. In case a tunable amplification frequency is required, a system such as a paramagnetic spin system where the frequency is determined by the strength of an applied static field can be used. An important possibility arises in this case. Since the excitation frequency is not necessarily the amplification frequency, it is possible to generate microwaves at frequencies higher than those of excitation. This is a possible approach to the problem of the generation (or amplification) of millimeter waves. Methods such as the molecular beam Maser that do not utilize rf electromagnetic excitation also offer a possibility for the generation of discrete frequencies in the millimeter and sub-millimeter region, by using transitions between relatively widely separated energy states. Vibrational transitions and certain rotational transitions, as, e.g., in ammonia, lie in the far infrared and sub-millimeter part of the frequency spectrum and might prove suitable.

Thus molecular amplifiers provide a means of achieving low noise amplification of microwaves. At present, bandwidths are quite low, but developments in the near future should greatly improve this situation. Below microwave frequencies, the gain fall-off with frequency will probably preclude their use; in the millimeter and sub-millimeter range, they offer new possibilities for amplification and generation. Many developments both in excitation methods and in molecular systems suitable for use in these devices can be expected in the near future.

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<sup>31</sup> Additional noise is introduced when the number of interacting molecules fluctuates in time. This is generally relatively unimportant.

## Appendix

Consider a molecule with two energy levels, with an oscillating microwave field  $E \cos(2\pi\nu t)$  inducing transitions between them. If the state function of the molecule is written as a linear combination of pure energy state functions, as in Eq. (1),

$$\psi = \sum_j a_j(t) \psi_j, \quad (1)$$

then the quantum mechanical equations for the time dependence of the  $a_j$ 's are given by:<sup>32</sup>

$$\frac{da_j}{dt} = \frac{2\pi}{ib} \sum_n W_{jn} a_n \exp(2\pi i \nu_{jn} t) \quad (26)$$

Here  $i = \sqrt{-1}$ ,  $\nu_{jn} = (W_j - W_n)/h$ ,  $W_j$  is the energy of the  $j$ th state, etc., and  $W_{jn}$ , the  $j$ nth element of the perturbation matrix, is given by

$$\begin{aligned} W_{jn} &\equiv \int \psi_j^* W \psi_n dv \\ &= \int \psi_j^* (pE \cos(2\pi\nu t)) \psi_n dv \\ &= E \cos(2\pi\nu t) \int \psi_j^* p \psi_n dv. \end{aligned} \quad (27)$$

The integral represents  $p_{jn}$ , the strength of the dipole moment coupling the states  $j$  and  $n$ .

In the two-state problem at hand, Eqs. (26) and (27) become

$$\begin{aligned} \frac{da_1}{dt} &= \frac{2\pi E \cos(2\pi\nu t)}{ib} [p_{11} a_1 + p_{12} a_2 \exp(2\pi i \nu_{12} t)] \\ \frac{da_2}{dt} &= \frac{2\pi E \cos(2\pi\nu t)}{ib} [p_{21} a_1 \exp(2\pi i \nu_{21} t) + p_{22} a_2]. \end{aligned}$$

Here  $p_{ii}$  indicates the dipole moment possessed by a molecule when it is in the state of energy  $W_i$ . Such static dipoles do not lead to resonant transition effects and will

be neglected; also  $p_{12} = p_{21} = p$ , in the cases of interest at present, so

$$\frac{da_1}{dt} \approx \frac{2\pi p E}{ib} \cos(2\pi\nu t) \exp(2\pi i \nu_{12} t) a_2$$

$$\frac{da_2}{dt} \approx \frac{2\pi p E}{ib} \cos(2\pi\nu t) \exp(2\pi i \nu_{21} t) a_1.$$

Also,  $\nu_{21} = -\nu_{12} = \nu_0$ , and defining  $\Delta\nu \equiv \nu - \nu_0$ ,

$$\frac{da_1}{dt} = \frac{\pi p E}{ib} \{ \exp[2\pi i \Delta\nu t] + \exp[-2\pi i(\nu + \nu_0)t] \} a_2$$

$$\frac{da_2}{dt} = \frac{\pi p E}{ib} \{ \exp[2\pi i(\nu + \nu_0)t] + \exp[-2\pi i \Delta\nu t] \} a_1.$$

The terms with  $(\nu + \nu_0)$  represent very high frequency perturbations on the basic behavior of the system. As they do not lead to any net transition effects over a reasonable averaging time, they can also be neglected, leading to

$$\frac{da_1}{dt} = \frac{\pi p E}{ib} \exp(2\pi i \Delta\nu t) a_2 \quad (28)$$

$$\frac{da_2}{dt} = \frac{\pi p E}{ib} \exp(-2\pi i \Delta\nu t) a_1.$$

It can be readily shown that the expressions

$$a_1 = \exp(\pi i \Delta\nu t) \left[ \cos \lambda t - \frac{\pi i \Delta\nu}{\lambda} \sin \lambda t \right]$$

$$a_2 = \frac{\pi i p E}{b \lambda} \exp(-\pi i \Delta\nu t) \sin \lambda t$$

satisfy the Eqs. (28) if

$$\lambda = \pi \left[ (\Delta\nu)^2 + \left( \frac{pE}{b} \right)^2 \right]^{1/2}$$

<sup>32</sup>L. I. Schiff, QUANTUM MECHANICS, McGraw-Hill Book Company, Inc., New York, N. Y., pp. 189-190, 1949.

Furthermore, at  $t = 0$  they reduce to

$$a_1(0) = 1$$

$$a_2(0) = 0 .$$

For such a molecule in energy state (1) at time  $t = 0$ , the probability that it has undergone a transition and is in

state (2) at time  $t$  is:

$$\begin{aligned} \text{Transition probability} &= |a_2(t)|^2 \\ &= \frac{\left(\frac{pE}{b}\right)^2 \sin^2 \left\{ \pi \left[ (\Delta\nu)^2 + \left(\frac{pE}{b}\right)^2 \right]^{1/2} t \right\}}{(\Delta\nu)^2 + \left(\frac{pE}{b}\right)^2} , \end{aligned}$$

which is Eq. (6) in the text.

