ABSORPTION SPECTROSCOPY USING OPTICAL MASERS

Including A Discussion Of Early Investigations Into The

Process Of Stimulated Emission Of Radiation

by

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Table Of Contents

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ABSTRACT

PART I: The historical development of masers is discussed in order to find out why they were not produced until the 1950's. It begins with the theoretical interpretation of the radiation process by Einstein in 1916. Then follows the quantum mechanical interpretations and experiments on the process of negative dispersion in the 1920's. In light of the technological advancements of World War II, the EPR work of Bloch and the negative temperature experiments of Purcell, Pound, and Ramsey examined. The proposal for the maser is reviewed and the subsequent development and extension of this device to optical frequencies is described.

Part II: Optical spectroscopic techniques in gases are studied. The complex susceptibility and absorption coefficient is calculated for the case of a Stark absorption cell in the limit of a Doppler broadened line. Resonance techniques are considered, and it is shown that an enhancement in sensitivity by a factor of 200 is possibile utilizing a two cavity technique; enhancements by a factor in excess of 10^4 are possible using a single cavity method. Molecular beams are examined as a means of reducing Doppler and collision broadening. The possibilities of spectroscopic techniques employing tuneable masers of GaAs type are also explored.

Thesis SUpervisors: A. Javan, Professor of Physics(Associate);G. de Santillana, Professor of Humanities.

PART I

"But the history of science is not restricted to the enumeration of successful investigations. It has to tell of unsuccessful enquiries, and to explain why some of the ablest men have failed to find the key of knowledge, and how the reputations of others has only given a firmer footing to the errors into which they fell."

James Clerk Maxwell
Inaugural Lecture as
Professor of Experimental
Physics, University of Cambridge
October, 1871

Section I: <u>Introduction.</u>

The maser is a device which makes use of the property of stimulated emission of radiation. Generally, an inverted population* and resonant cavity are employed. The resulting energy radiated is highly monochromatic and coherent.

An inverted population occurs when more than half at the molecules of the molecules of a substance are in the higher of two possible energy levels. A resonant cavity is a physical structure which selectively enhances only a few modes of electromagnetic radiation. This selection occurs because of the boundary conditions imposed upon the electromagnetic radiation by the structure. As a result, only a few modes of oscillation produced by the emissive transitions of the inverted population are possible.

The gas maser is a simply constructed maser oscillator consisting of two parallel reflecting surfaces between which a discharge tube containing a low-pressure mixture of helium and neon is supported. The discharge is energized by a 50 watt r-f generator. The physical simplicity of the system leads one to wonder why such an arrangement was not constructed at a far earlier date than the fall of 1960. The properties of Fabry-Perot reflectors have been understood since the turn of the century, and gas discharges of similar nature were thoroughly investigated in the early 1930's. In fact, one might conjecture that at this particular period "the time was ripe". The existence of a mono-chromatic optical source would certainly have been of value to the intensive spectroscopic studies which were then in progress.

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*In the Raman effect radiation is emitted only when the population is not inverted. Masers can be constructed which utilize this principle.

In tracing the development of the maser, one must examine the early stages of the development of modern physics. The discussion begins with the theoretical interpretation of the radiation process by Albert Einstein in 1916 and 1917. It then notes the quantum mechanical interpretation of the process of optical dispersion in the mid-1920's. On the experimental side, several experiments which measured population inversions and their related effects in the 1930's and later shall be examined. The negative temperature experiments of Purcell, Pound , and Ramsey will be mentioned. The microwave work of Charles Townes and others which finally led to the construction of the first microwave maser in 1955 shall be discussed. Finally, the logical connections which were necessary for the development of optical and infrared masers will be discussed.

Throughout this work an effort has been made to eliminate much of the mathematics which so often obscures insight into the problem at hand.

Section 2: Early Theoretical Developments

In the year 1900 Max Planck correctly predicted the energy spectrum of a radiating black body by postulating a discrete energy distribution for the system. The subsequent development of the Bohr spectral theory in 1913 was a more elaborate conception of the atom which gave a physical interpretation to the nature of the radiative process. The Bohr theory implied that discrete transitions could occur from a lower energy level to a higher one, as well as in the reverse direction. In 1916, and then in more detail in 1917, Albert Einstein developed[2] the connection between the Planck law and the Bohr theory, laying the theoretical groundwork for the principle of maser operation.

Einstein considered a system with two energy levels between which radiative transitions could occur. He assumed the two levels to be in a bath of radiation with a component $E_j - E_i$ with E_j chosen as the upper level. It might appear as if three distinct radiative events could occur between levels. First, a photon might be spontaneously emitted from the upper level, E_j , and absorbed by the lower level E_i . Second, through interaction with a field a photon could be transported from E_i to E_j thus raising the energy of the state by one quantum of energy(stimulated absorption.) Finally a photon could be transported from E_j to E_i, thus lowering the energy of the state by one quantum of energy(stimulated emission.) Einstein identified a probability coefficient with each process. It is noted in passing that the introduction of these coefficients marked the first systematic introduction of probability factors in the mathematics of quantum mechanics.

According to the law of detailed balancing, each elementary process must be counterbalanced by its inverse in order to maintain thermodynamical equilibrium. Einstein therefore interpreted

the two kinds of emission, spontaneous and stimulated, as part of

the same process and balanced them against the stimulated absorption.

This interpretation seemed rather strange at the time, in view of the fact that

stimulated emission seemed to be distinct from spontaneous emission. Only

when the detailed electrodynamical situation was considered by Dirac[3] in

1927 were these processes shown to be different aspects of the same process.

Section 3: Negative Dispersion in the 1920's and 1930's

The implications of Einstein's considerations to the spectroscopy of gases were first realized by Kramers[4] in 1924, and further developed by Kramers and Heisenberg[5] and then Bohr, Slater, and Kramers[6].

Dispersion is the phase change which occurs when a beam of light passes through a "dispersive" medium. Classical theory describes a dispersive medium as an assembly of microscopic damped harmonic oscillators. The resulting equation for the dispersion involves only a single expression corresponding to the response of these virtual oscillators to an electromagnetic field. This assumption is not a bad one for many experiments have shown that the interatomic potential is very close to harmonic for small disturbances. Furthermore, from quantum mechanical considerations it can be shown that any radiating dipole behaves like a radiating harmonic oscillator.

In a simple physical picture of the dispersion process one considers the external light of a particular frequency which falls upon an assembly of virtual oscillators of the dispersion medium. The radiation sets the oscillators in motion with a corresponding loss of intensity(or absorption.) However, when Einstein's considerations are taken into account a negative term must be added to the dispersion equation. Put in classical terms one might say that when a beam of light is incident on an assembly of atoms , some of them will begin to vibrate and absorb the radiation, while others will somehow vibrate "negatively", producing a negatve or reversed component of dispersion.

This picture of "negative virtual oscillators" was first suggested by Kramers in a letter to Nature in 1924.[4] In this letter he coined the phrase "negative dispersion" which was to become well known in the years that followed.

Starting in 1925 much experimental effort was focused on verifying new developments in physics. On the basis of the quantum mechanics a number of discrepancies which had occurred between experiment and the Bohr-spectral

theory could be accounted for.   A wealth of experiments suggested themselves.
Physicists were interested in investigating such phenomena as the lifetime of
excited states, atomic structure, the vector model of the atom, LS and jj coupling,
and the occupation of energy levels in gases.   Many of these experiments involved
spectroscopic techniques and spectroscopy became one of the powerful experimental
methods of the 1920's and 1930's.

Beginning in the 20's Ladenburg and his collaborators performed a
number of experiments using hydrogen and neon and other gases. In particular,
in an experiment in 1928 Carst and Ladenburg[7] tried to measure accurately a
discrepancy which had previously shown up[8] between expimental determination
of relative intensities in excited gases and theoretical values predicted by a
dispersion formula[9] that Ladenburg himself had advanced in 1921.

It should be mentioned that the actual measurements Ladenburg and
his colleagues performed were dispersion measurements.   In such experiments
the light source is split into two beams by a half-silvered mirror. One beam
passes through the absorbing gas and the other through an equal optical path-
length of a non-dispersive medium.   The two beams are then brought back
together and the interference pattern observed.   By measuring the phase shift
between the source and the light transsmitted through the gas, the intensity(and
therefore the relative population of various energy levels) can be determined
using the Kramers-Kronig relations[10] developed in 1927.

The result of the Carst-Ladenburg measurements was that the phase
change detected as a function of frequency was smaller than that change given by
the Ladenburg expression.   It could be explained , however, on the basis of the
Kramers dispersion theory.   What this meant in terms of relative population
of energy levels was that, in addition to the usual absorptive transitions, a
number of competing emissive transitions were taking place, having the effect
of decreasing the net absorption.

This was the first experiment in which negative dispersion was noted. Further experiments were made throughout the thirties by both the Ladenburg group[11] and other workers. They tried to increase the effect of negative dispersion in several ways, including increasing the pressure and excitation level of the gas. In every case ,however, they found that the inverted population was small and existed in the presance of a larger uninverted population.

Ladenburg's interest in negative dispersion seems to have lasted over a period of about five years, culminating in a review article[12] in the newly introduced <u>Reviews of Modern Physics</u>. There were a large number of other phenomena to be investigated, however, and it is not surprising that he eventually turned to other areas.

Other spectroscopists of the 1930's also noticed negative dispersion. Oldenberg,[13] while working with OH ions appears to have noted an inverted population on several occasions in 1934 and 1936, **but** appears not to have pursued this work.

Houtermans,[14] in 1960, recounts having observed negative dispersion in his work on the predissociation of molecules in 1932. He explained this in terms of a "photon avalanche" and even considered constructing a single pass amplifier based on the effect. But he was eventually discouraged from this work by colleagues, and never returned to it.

There are several important points concerning these early negative dispersion experiments which should be noted:

1. The effect of negatve dispersion had been observed independently by at least several physicists.

2. In every case, the inverted population was small and existed in the presence of a larger uninverted population.

3. The discovery of negative dispersion represented an important verification of the newly developed quantum theory.

4. The possibility of further applications of this phenomenon were scarcely consider

Section IV: The War and Postwar Developments.

With the passing of the 1930's, the areas of interest to physicists changed.   A primary reason for this change was the advent of World War II.   The role of science was relatively minor in World War I.   As an illustration, upon entry of the United States into the war, the American Chemical Society wrote a letter to the War Department offering its services. The War Department declined explaining that it already had a chemist.[15] The situation in World War II was quite different.   During the war there were many scientists working for the government on military applications and making technological achievements in the fields of jet propulsion, radar guidance systems, and the atomic bomb.

Two important consequences of the war from the present point of view were the merging of electrical engineering and physics,[16] and the invention of radar.[17] This point shall be returned to in a later section, but it is mentioned in passing that a familiarity with electrical engineering techniques acquainted the physicist with the process of regeneration, while the techniques of radar brought familiarity with the theory and application at microwave, the phenomenon at resonance, and the resonant cavity.

Freed from their wartime scientific responsibilities, and filled with technological momentum, physicists were anxious to turn their attention to the many new areas that had been uncovered during the war years.   One of the first post-war developments in physics was the successful exploration in 1946, of the phenomenon of electron paramangetic resonance by Bloch.[18] This was made possible by advanced microwave technology developed during the war.   The theoretical and experimental success of Bloch's work led to an understanding of the phenomenon of paramagnetic resonance in solids

which is the analog of absorption in gases.

Bloch, in the course of his work, apparently achieved a population inversion, but did not attach any importance to it. It remained for Purcell, Pound, and Ramsey to demonstrate conclusively the possibility of total population inversion. The "negative temperature" experiments they performed represent the first deliberate attempt to produce net inverted population. Before going into their work, the concept of negative temperatures is briefly discussed.

According to the Boltzmann statistical distribution, when a system is in thermodynamical equilibrium, the number Ni of atoms in the corresponding energy state Ei is distributed exponentially as a function of energy:

$$N_i \sim e^{-E_i/kT}$$

The population ratio between two states Ei and Ej, where we define Ej   Ei is given by

$$\frac{N_j}{N_i} = e^{-E_j-E_i/kT}$$

It is thus mathematically convenient to measure the relative population of two energy levels in terms of temperature:

$$T = \frac{E_j - E_i}{k \ln(N_j/N_i)}$$

The population of spin systems has been measured in this way at least as early as 1938.[19] Usually Nj $>$ Ni and the temperature is a positive quantity. However, in the event that the population is inverted, the temperature will be negative[*].

The initial experiment which produced negative temperatures was carried out by Purcell and Paund in the latter part of 1950. A crystal of lithium fluoride was placed in a strong magnetic field in order to align the

nuclear spins. When the system reached steady state, the crystal was removed from the field and the spins inverted with respect to the field in a time interval short compared to the Larmour precession period. The crystal was then replaced in the field and the demagnetization was measured. For about five minutes, the spins returned to steady state, passing from the negative into the positive temperature region.

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*Some intersting properties of negative temperatures should be mentioned. Negative temperatures are "hotter" than "ordinary" temperatures, giving up heat when they are brought into thermal contact with bodies of positive temperature. As the body passes from negative to positive temperature, it passes through infinite temperature. An attempt has been made by Ramsey[21] to generalize the laws of thermodynamics to include the effects of negative temperature. Care must be excerised in dealing with them, however, since it is not at all clear that there is physical significance associated with them.

Section V: Comparison of the 30's and the 50's: Some Conclusions.

We now come to a central issue in the development of the maser. The

scientists of the 1930's had technology sufficiently developed to construct

an optical maser of the gaseous type. They had thoroughly explored the

properties of gas discharges; Fabry-Perot interferometers of high quality

22

could be constructed. Yet it was thirty years later that the optical maser

came into being. At this stage it may be useful to approach the problem from

a different point of view. Let us compare the work on absorption in gases in

the early thirties with the study of electron paramagnetic resonance and

related phenomena in solids in the late forties and early fifties. Some

similarities are immediately evident. Both phenomena exhibit similar kinds

of phase and amplitude relations. In both cases absorption was initially

of interest, and the realization that emission was possible followed later in

both cases.

There are also important differences. One lies in the characteristics

of the two media. Under normal conditions, inversion of population in gases is

a small effect occurring in the presence of a larger absorption. In solids,

on the other hand, it is relatively easy to produce a net population and in some

cases, total inversion is possible. We shall return to this point presently.

A second important difference is that the two studies were conducted during

different eras of scientific interest. The physicists of the early thirties

were carried along with the wave of new developments in quantum theory. They

were immersed in the problem of predicting and verifying the properties of

atoms and molecules and their interactions with radiation which could not be

predicted from the Bohr spectral theory. They investigated such areas as the occupation of energy levels in gases, the lifetimes of excited states, and the structure of atoms. The physicists of the late forties more or less understood these problems; that is to say, the more easily solvable problems had been resolved. Physicist' interest in optical spectroscopy thus declined, and the techniques developed in this field were applied to the realm of chemistry and physical chemistry.

The physicists of the late forties were largely motivated by the scientific consequences of World War II. In particular, two changes which are important in the present context were the merging of physics and electrical engineering and the rapid development of microwave technology. The origin of microwave technology can be traced to the development or radar; the merging of physics and electrical engineering was a more comprehensive change, due not so much to any particular technique as to a new attitude towards physics and its relationship towards technology. Both changes stimulated interest in the phenomenon of resonance.

Rephrasing the original question, one can ask why the optical gas maser was not a natural outgrowth of the work of Ladenburg, Oldenberg, and their colleagues. Was it only an "accident" that they did not hit upon the principle of maser action, or would it have been an accident if they had hit upon it? Perhaps the answer to this question is related to the fact that in the thirties the scientisits were talking about absorption in gases while in the fifties they they referred to paramagnetic resonance in solids.

There are two ~~more~~ requisites for maser action: (i) the creation of an inverted population, and (ii) the utilization of a suitable resonator to enhance the coherence of the radiation emitted as a result of population inversion. The possibility of hitting upon the principle of maser action is strongly dependent upon a thorough understanding of the concepts presented by (i) and (ii).

As far as condition (ii) is concerned, the phenomenon of resonance was being dealt with and ~~that~~ the interest level was high in the late forties and the fifties. On the other hand, this area was of no particular interest in 1930. The situation with regard to requisite (i) is more complex. Greater population inversions are realizeable in solids than in gases, although this fact alone does not show that the maser was not feasible in 1930, since both gaseous and solid media have subsequently been used as sources of population inversion. The scientists of the 1930's were aware of population inversion as a valid quantum mechanical effect which accounted for certain discrepancies between experiment and older theory, nevertheless, they failed to extend the idea beyond this. Perhaps the reason for this is that they were not really comfortable with the concept of a non-thermodynamical process. A scientist in 1930 would, of course, recognize the fact that negative dispersion led to a non-thermodynamical situation (in the sense that the population of molecular energy levels deviates from the Maxwellian distribution). But in their experimental situations the deviation was small and the full import of negative dispersion was never forced into the open.

Contrast this with the situation in 1950: the dramatic demonstration of Purcell, Pound, and Ramsey was that total population inversion is possible. This brought home, with full force, the fact that non-thermodynamical equilibriums (appropriately measured in "negative" temperatures) were

important physically realizable situations which could be worked with, and perhaps, harnessed to do useful work.

We, therefore, suggest that at the core of the situation, the reason that the principle of maser action was not proposed in the 1930's because of the mental climate of the science of the times the particular prejudices which characterized the physics of the 1930's. Ladenburg and his colleagues knew of the Fabry-Perot <u>interferometer</u>, not of the Fabry-Perot <u>resonator</u>. They dealt with the <u>absorption</u> of gases, not with the <u>resonance</u> properties of them; and although they recognized the existence of non-thermodynamical situations, they were unable to deal with them. It is therefore understandable that the principle of maser action was not conceived of in 1935. Although the necessary technology for construction of an optical maser of the Helium-Neon type was at hand, the time was not ripe for the invention. By the same token, the invention of the maser can be understood in terms of the natural evolution of scientific thought in the late forties and early fifties.

Section 6: Development of the Microwave Maser

By the end of the 1940's, am understanding of the two conditions necessary for molecular amplification had been attained. First, physicists had become familiar with the concepts and methods used in microwave technology; they had attained an understanding of the resonance phenomenon and the resonant cavity. Secondly, it was a well established experimental fact that total population inversion was possible. Consequently, it is not surprising that within a year, three independent proposals for the maser were made. Prior to that time, population inversion had been achieved, but no net gain or amplification had been observed.

The first proposal came from C.H. Townes,[23] in May, 1951. He proposed that the upper inversion states of a beam of ammonia molecules be selectively focused by a non-uniform static electric field, and then directed into a resonant cavity, in which downward transitions could be induced, thus emitting coherent microwaves.

Independent proposals came from N. G. Basov and A. M. Prokharov[24] of the Soviet Union*in May, 1952, and J= Weber,[25] in June, 1952. Weber's proposal, unlike the other two, did not make use of the resonant cavity.

In 1954 and 1955, succesful amplification[27] and oscillation[28] of microwaves were reported by Townes and co-workers. The molecular amplification achieved by Townes thus represented a synthesis of ideas that can be traced to the early years of the present century.

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* The Soviet Union cites as a pertinent reference to inverted populations, the doctoral thesis of V.I. Fabricant, written in 1940. The refernce can be found in footnote[26].

Section 7: The Development of the Optical Maser

Once the ammonia maser had been made to operate, phsyicists attempted to extend maser techniques to the visible and infrared regions. The problem they faced was one of mode selection. Population inversions were known which would radiate visible light; to support this inversion, howev r, it seemed necessary to have a resonant cavity which would enhhance one or at the very most several modes. A cavity of this kind would have to have physical dimensions the order of a wavelength of the radiation. It therefore seemed that coherent light below one centimeter wave length could not be produced. *

The situation was finally resolved in 1958 when Townes and Schawlow [29] proposed using a multimode optical cavity of the Fabry-Perot type; that is, the plane parallel mirrors. The problem of mode selection in this case was shown to be easily solvable. Workers immediately began to apply this idea, and in 1960 a continuous wave optical maser had been constructed by A. Javan [30] which employed the inverted population within a gas discharge(of helium and neon) of the kind well known to Ladenburg and his colleagues. †

There is a span of about five years between the development of the microwave maser and the subsequent proposal for the optical maser. The question now to be raised is why the connection was not immediately made betwe

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* A typical attidute was expressed by Hans Mueller of M. I. T. as far back as 1930. [31] Dr. Mueller lectured his optics students that it would be possible to produce coherent radiation at wavelengths of several cm. but that the resonant cavities required to produce visible light would be impossible to construct because of their microscopic dimensions. He stated that "if someone could train the atom to emit coherently in the visible region it would represent a sizeable achievement."

† A pulsed solid state optical maser was announced by Maiman [32] in 1959.

resonant microwave cavities and resonant optical cavities. A part of the answer lies in the problem of mode selection. There is another point, however, which must be noted. The Fabry-Perot interferometer was well known since 1898. It was introduced, though, as an interference device and was not thought of as a resonant structure. It was only when the realization of its application as a resonator was made that it could be applied to the maser principle. This, then, was the underlying significance of the Downes - Schawlow proposal, and can help to account for the delay between microwave and optical masers.

Conclusion

With the helium-neon maser of Javan the connection finally was completed between the negative dispersion experiments of the 1930's and the principle of maser action. It has been seen that structures of the helium - neon type were not previously developed because of three reasons:

1) The full recognition of population inversions was not m ade until 1950.

2) Resonance techniques did not suggest themselves in the 1930's.

3) The Fabry_Perot device was thought of an an interferometer and not a resonator.

At first glance it might appear that the failure to develop a maser in the 30's was mere "bad luck". It has been the thesis of Part I that in fact, in view of the interests and attitudes of physicists at that time, times were not "ripe" in the 30's. It is understandable that the ideas fundamental to the maser did not suggest themselves then.

FOOTNOTES :PART I

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PART II

Chapter I: Some Aspects of the Process of Absorption

Section 1: General Considerations.

The process of absorption of electromagnetic energy in a molecular gas may correspond to photon transitions between rotational and vibrational levels. At microwave frequencies the transitions generally occur between nearby rotational levels; in the optical region the level spacing is larger and absorption lines may correspond to transitions between different rotational and vibrational states.

High resolution details of absorption at optical frequencies can lead to a wealth of information, including knowledge about molecular collisions, matrix elements, and information about atomic and molecular wave functions. Such resolution can be obtained by utilizing continuous-wave optical and infrared masers in spectroscopic techniques.

One technique which immediately suggests itself is sweeping the frequency of the electromagnetic radiation through the resonance of the gas and observing the intensity change resulting from the molecular absorption. Resolution is limited by the frequency breadth of the source.

Prior to the advent of the optical maser, the utility of this technique was limited since no coherent sources were available. It has long been utilized in the microwave region, however, since monochromatic sources have been available since 1946[1]. Unfortunately, the limited tuneability of optical masers prevents the direct application of the technique in the optical region.*

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* This technique may be feasible with the gallium arsenide maser-diode.

See Section 6.

However, the number of discrete frequencies at which optical masers oscillate is large. For example, over 70 different transitions in the optical and near infrared have been made to oscillate so far in the helium – neon maser alone. At the present state of the art, a large number of optical absorption lines can be closely approached. This suggests the related technique of choosing a maser transition, and then shifting the absorption line itself by utilizing either Stark or Zeeman tuning.

The Stark effect is usually experimentally more suitable for our purposes.* Considerations from perturbation theory[2] show that certain molecular energy levels present a first order Stark shift given by

$$\Delta W = \mu E \frac{MK}{J(J+1)} , \qquad (1.1)$$

where J is the quantum number corresponding to total rotational angular momentum, K is the quantum number corresponding to the projection of $\underline{J}$ on the molecular axis, and M is the quantum number corresponding to the projection of $\underline{J}$ on any fixed spatial axis; μ is the electric dipole moment and $\underline{E}$ is the electric field.

Transitions can occur between levels, following the selection rules

$$\begin{aligned} J &= \pm 1 \\ K &= 0 \\ M &= \pm 1, \ 0 \end{aligned} \qquad (1.2)$$

The frequency of such transitions is given by

$$h \nu_{STARK} \sim \Delta W(J,K,M) - \Delta W(J',K,M') \qquad (1.3)$$

A typical value of μ is a few debeyes (1 debeye = 10^{-8} e.s.u.). Choosing an electric field of 2 Kilovolts per centimeter (7 e.s.u.), we obtain from equation (1.1)

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* In cases where the upper state is other than $^{1}\Sigma$, particular levels may present sizeable magnetic dipoles, in which case magnetic tuning may be possible.

$$\nu_{STARK} \approx 1 \ KMC/SEC \qquad (1.4)$$

Hence, if a maser transition can be found within 1 kilomegacycle per second of the absorption line in question, this high resolution technique will be applicable.

In principle, much higher fields may be applied, with a corresponding increase in the frequency shift of the spectral line. The practical limitation is, of course, the breakdown of the Stark field, which becomes more likely at high pressures. One must choose a pressure low enough to support a large Stark field, and yet sufficiently high to yield a strong absorption signal. It will be shown that certain spectroscopic techniques can increase the sensitivity to absorption, enabling extremely low pressures to be realized. Consequently, much greater Stark fields can be applied, thus extending the range of the technique.

Spectral Line Shape:

Details of shape and width of an absorption line depend upon a number of factors. A single, undisturbed and motionless molecule would absorb energy only over a very narrow range of frequencies. In a gas, we must associate a natural lifetime with each excited state. Because the molecules are in constant motion, Doppler broadening occurs. Because they are constantly colliding with one another, they undergo collision (or pressure) broadening. It is of interest to estimate the magnitudes of these various effects.

Natural Broadening:

In any radiative process, there is an inherent natural lifetime, τ_n, during which a photon may be absorbed or emitted. It is, in principle, impossible to localize the exact time within the interval when the photon was

absorbed, without suffering a corresponding decrease in information about the localization of its energy. The Einstein A coefficient, which is the reciprocal of τ_n, is given by

$$A = \frac{64\pi^4 \mu^2}{3h\,\lambda^3} \quad , \qquad (1.5)$$

where λ is the wavelength at which the radiation is spontaneously emitted, and μ is the matrix element connecting the two levels. The natural broadening is Lorentzian. For a typical value of μ (5 debeyes) and a wavelength of one micron,

$$\Delta\nu_n = \frac{A}{2\pi} \approx 1.2 \text{ mc/sec.} \quad . \qquad (1.7)$$

Collision broadening:

On the basis of kinetic theory, we can associate a collision lifetime,   , with the molecules in a gas:

$$\tau_c = \frac{1}{\sqrt{2\pi}\ \nu_c\,\sigma\,n} \quad , \qquad (1.8)$$

where ν_c is essentially the mean velocity (there is a small correction factor), n is the molecular density of the gas, and σ is the scattering cross section. The number of collisions is distributed exponentially in time:

$$n(t_0) = \frac{dt_0}{\tau}\, e^{-(t-t_0)/\tau} \quad , \qquad (1.9)$$

where $n(t_0)$ is the probability that the molecule made its last collision between $t-t_0$ and $t-t_0+dt_0$. From this it can be shown that the broadening will be Lorentzian[3], with a breadth

$$\Delta \omega_c = \sqrt{2} \, v_c \, \sigma n .$$

(1.10)

It is evident that collision broadening is a pressure dependent process. At room temperature, the molecular density, n, is related to the pressure, p(mm. Hg.), by

$$n \approx 3 \times 10^{16} \cdot p .$$

(1.11)

The cross section, σ, might be of the order of 10^{-15} cm.^{2}, and consequently, at room temperature, we expect a broadening of the order

$$\Delta v_c \approx 25 - 30 \, Mc/sec/mm \, Hg.$$

(1.12)

Doppler broadening:

Because the gas molecules are in motion, the radiation they emit and absorb will have a spread in frequency distribution. Suppose that the molecule has a component of motion along the direction of the observer (the photodetector in the present case.) Then it will undergo a frequency shift

$$\Delta \omega_D = \omega_0 \cdot \frac{v}{c} ,$$

(1.13)

where v is the velocity component in the direction of the observer, and ω_0 is the radiation frequency of the molecule at rest. The distribution of velocities is Maxwellian:

$$n(v) = \frac{n}{u\sqrt{\pi}} e^{-v^2/u^2} .$$

(1.14a)

where

$$u^2 = \frac{2KT}{M} .$$

<div align="right">(1.14b)</div>

Substitution of equation 1.11 into equation 1.12, yields the distribution as a function of frequency:

$$n(\omega) = \frac{n}{(\omega_0/c)\sqrt{\pi}} \, e^{-\left(\frac{\omega-\omega_0}{\Delta\omega_D}\right)^2} ,$$

<div align="right">(1.15)</div>

which is Gaussian with a half-width at half-maximum

$$\Delta\omega_{\frac{1}{2}} = \omega_0 \cdot \frac{u}{c}\sqrt{\ln 2} .$$

<div align="right">(1.16)</div>

At room temperature $\Delta\omega_{1/2}$ will be of the order of 400 megacycles per second.

It is clear that at pressures below 10 millimeters of mercury, the spectral width will be completely determined by equation 1.16 (figure 1.2). It is therefore of interest to consider a technique for reducing $\Delta\omega_D$. Such a consideration is carried out in section 6.

ChapterII: Methods For Optical Maser Spectroscopy

Section 2: Stark Absorption Cell

In this section we shall develop in some detail the considerations

outlined in section 1. Consider the arrangement illustrated schematically

in figure 2.1. The beam of a continuous - wave optical maser passes through

the transparent end-windows of a Stark absorption cell and impinges upon

a photodetector.

The Stark cell is essentially a parallel plate capacitor, arranged so that

the optical beam passes through the strong electric field produced between

the plates. In principle a D.C. field may be applied. The signal to noise

ratio can be sizeably enhanced however, by applying a sinusoidal signal of

several kilocycles per second. In this situation, the absorption signal is

modulated, but the scattered light is not. The output is then fed into a

receiver tuned to the modulation frequency. In this way most of the

absorption signal is passed while most of the noise is rejected. Hence the

signal to noise ratio is increased.

Susceptibility:

If the molecules in a gas are polarizable in an electric field, $E(\omega)$,

we can associate a complex susceptibility, χ, with the gas as a whole.

In general, χ will be a function of the frequency of the electric field, as

well as the molecular resonant frequency. We therefore define

$$\chi(\omega, \omega_0) \equiv \chi' + i\chi'', \qquad (2.1)$$

where ω_0 is the resonant frequency of the molecule. The relationship between

χ and the polarization P (the dipole moment per unit volume) is given by

STARK POWER SUPPLY

TUNED RECEIVER

STARK ELECTRODE

INVERTED POPULATION

CAVITY MIRRORS

OPTICAL MASER

GAS INLET

OUTLET TO VACUUM SYSTEM

PHOTO-DETECTOR

GAS ABSORPTION CELL

(QUARTZ WINDOWS)

RECORDER
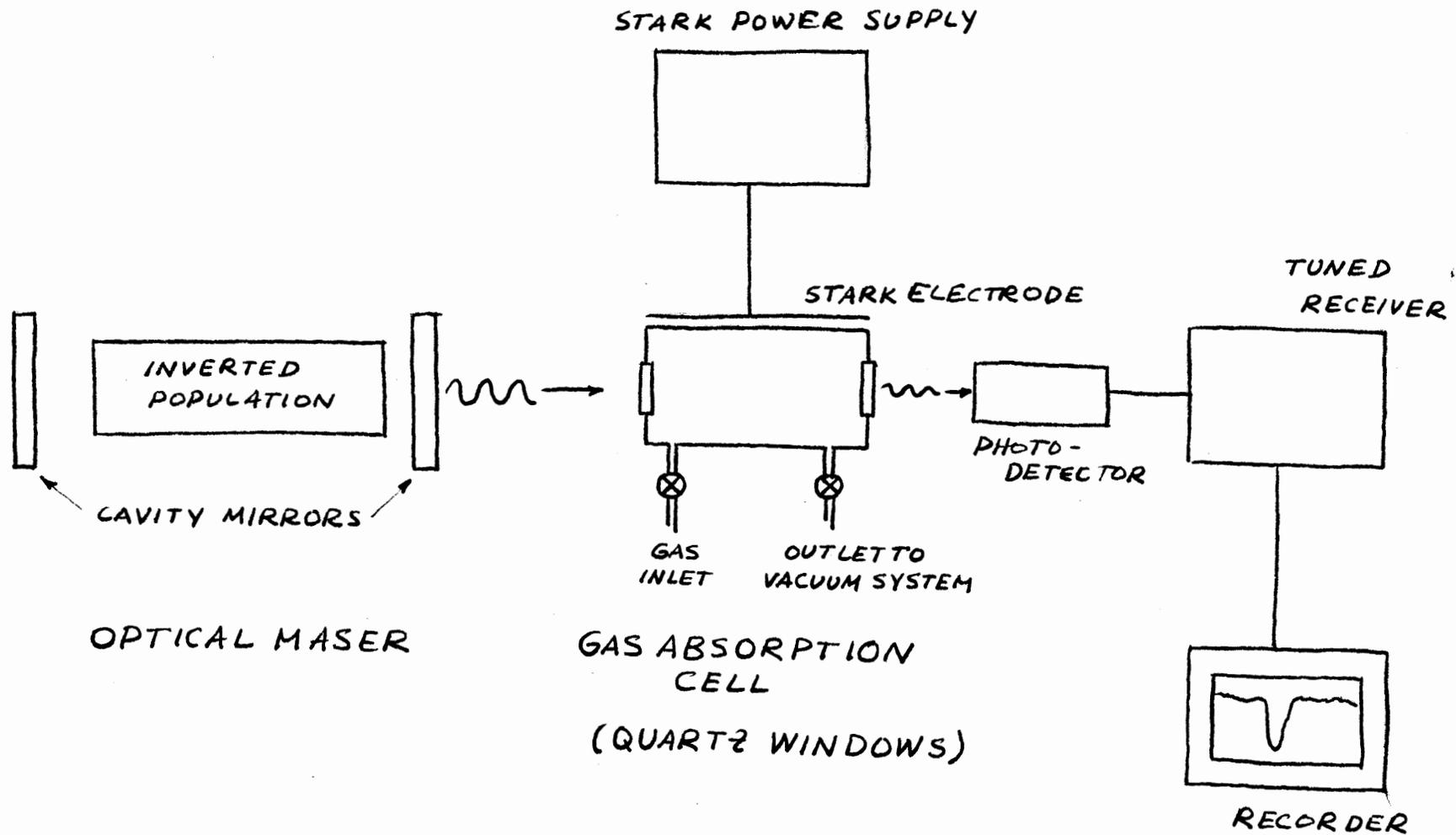
SINGLE PASS ABSORPTION EXPERIMENT

FIGURE 2.1

$$\underline{P} = \mathcal{X} \underline{E} . \qquad\qquad (2.2)$$

The susceptibility, $\mathcal{X}$, contains information about both the phase relationship and amplitude of the absorption of electromagnetic energy from the field by the molecules of the gas.

Absorption coefficient:

The absorption coefficient, γ, is defined such that

$$I(x) = I_o e^{-x\gamma} , \qquad\qquad (2.3)$$

where $I(x)$ is the intensity of the radiation after it has traversed a distance x, and $I(0) = I_o$. If the loss is small, then

$$\frac{\Delta I_L}{I_o} = \gamma x , \qquad\qquad (2.4)$$

where we have defined $I_L = I_o - I(x)$ as the intensity loss in an interval x. Also, since intensity is proportional to power,

$$\frac{\Delta P_L}{P_o} = \gamma x , \qquad\qquad (2.5)$$

where P_L is the power loss in the interval x and P_o is the initial power. Power loss may be expressed in terms of the polarization $\underline{P}$ and the Electric field, $\underline{E}$.

$$\Delta P_L = \dot{\underline{P}} \cdot \underline{E} . \qquad\qquad (2.6)$$

Also, the time average of the total power per unit area , P_a, may be written as

$$P_a = \frac{c}{8\pi} E_o^2 . \qquad\qquad (2.7)$$

Using equations 2.5, 2.7, 2.1 and 2.2, and the fact that

$$\langle AB \rangle_{time} = \frac{1}{2} Re(A*B) \qquad (2.8)$$

we finally obtain the absorption coefficient as a function of χ'':

$$\gamma = -4\pi \frac{\omega}{c} \chi''. \qquad (2.9)$$

<u>Calculation of χ and γ</u>:

In order to obtain a solution of equation 2.9, it is necessary to express χ in terms of the physical characteristics of the gas molecules. Such an expression may be obtained on the basis of the time - dependent perturbation theory[4]. The details are treated in Appendix A and the results, including the saturation effect, are quoted here:

$$\chi = \frac{n\mu^2}{\hbar} \left\{ \frac{(\omega - \omega_0) - i' \Delta\omega_c}{(\omega - \omega_0)^2 + (\Delta\omega_c)^2 + \left(\frac{\mu E}{\hbar}\right)^2} \right\}. \qquad (2.10)$$

Equation 2.10 has already been averaged over t_o, the time elapsed since the last collision. Substitution of equation 2.10 into equation 2.9, yields the result that is well known in the microwave region:

$$\gamma = \frac{8\pi^2 \mu^2 n \omega}{c\hbar} \cdot \frac{\Delta\omega_c}{(\omega - \omega_0)^2 + (\Delta\omega_c)^2 + \left(\frac{\mu E}{\hbar}\right)^2}, \qquad (2.11)$$

where $\Delta\omega_c$ is the collision width introduced in equation 1.8, μ is the dipole matrix element of the transition, $\underline{E}$ is the electric field of the maser beam, and n is the density of molecules in the lower of the two states involved in the transition. The quantity n will be discussed in Appendix B.

It is important to note that equation 2.11 is valid only if the Doppler width is much smaller than the collision width; i.e., if

$$\frac{\Delta\omega_D}{\Delta\omega_c} \ll 1. \qquad (2.12)$$

From the order of magnitude estimates given in section 1, it is seen that

at room temperature,

$$\Delta \omega_D \approx 400 \text{ Mc}/\text{sec}$$

and

$$\Delta \omega_c \approx 25 \text{ Mc}/\text{sec}/\text{mm Hg}. \qquad (2.13)$$

Hence equation 2.11 will be valid at pressures larger than 100 millimeters

of mercury.* However, for pressures of the order of 10 millimeters of

mercury and lower, condition 2.12 is violated. In order to obtain a realistic

description of the line shape, Doppler broadening must be included in the

expression for the susceptibility. We must, therefore, average χ, which is

given by equation 2.10, over the Gaussian distribution given by equation 1.15:

$$\langle \chi \rangle = \frac{\mu^2 n}{\hbar \Delta \omega_D \sqrt{\pi}} \int_{-\infty}^{\infty} \frac{(\omega - \omega') - i \Delta \omega_c}{(\omega - \omega')^2 + (\Delta \omega_c)^2 + \left(\frac{\mu E}{\hbar}\right)^2} e^{-\left(\frac{\omega' - \omega_0}{\Delta \omega_D}\right)^2} d\omega' \qquad (2.14)$$

where ω' is the variable of integration, and ω_0 is the center frequency of

the Doppler-broadened line. This integration has been carried out[5];

the result is

$$\chi' = \frac{2 \mu^2 n}{\hbar \Delta \omega_D} e^{-\left(\frac{\omega - \omega_0}{\Delta \omega_D}\right)^2} \int_0^{\frac{\omega - \omega_0}{\Delta \omega_D}} e^{x^2} dx \qquad (2.15)$$

$$\chi'' = -\frac{\mu^2 n}{\hbar \Delta \omega_D} \sqrt{\frac{\pi}{7 + \left(\frac{\mu E}{\hbar \Delta \omega_c}\right)^2}} e^{-\left(\frac{\omega - \omega_0}{\Delta \omega_D}\right)^2} \qquad (2.16)$$

---

* In the microwave region, pressure broadening limits the resolution in

almost all cases of interest.

Substitution of equation 2.16 into equation 2.9 yields an expression for γ:

$$\gamma = \frac{8\pi^2 w}{c} \frac{\mu^2 n}{\hbar \Delta w_D} \sqrt{\frac{\pi}{1 + \left(\frac{\mu E}{\hbar \Delta w_c}\right)^2}} \; e^{-\left(\frac{w - w_0}{\Delta w_D}\right)^2} \tag{2.17}$$

The range of validity of equation 2.17 is given by:

$$\frac{\Delta w_D}{\Delta w_c} \gg 1 \tag{2.18}$$

Discussion of absorption line shape:

We will now investigate the behavior of γ. For ease of comparison, equations 2.11 and 2.17 are rewritten:

$$\gamma_c = \frac{8\pi^2 \mu^2 n w}{c \hbar} \cdot \frac{\Delta w_c}{(w - w_0)^2 + (\Delta w_c)^2 + \left(\frac{\mu E}{\hbar}\right)^2} \tag{2.11} \quad p > 100 \text{ mm Hg}$$

$$\gamma_D = \frac{8\pi \mu^2 n w}{c \hbar \Delta w_D} \sqrt{\frac{\pi}{1 + \left(\frac{\mu E}{\hbar \Delta w_c}\right)^2}} \; e^{-\left(\frac{w - w_0}{\Delta w_D}\right)^2} \tag{2.17} \quad p < 10 \text{ mm Hg}$$

where the subscript on γ indicates its predominant source of broadening.

Unsaturated case:

Consider the case in which

$$\left(\frac{\mu E}{\hbar \Delta w_c}\right)^2 \ll 1 \tag{2.19}$$

Equations 2.17 and 2.11 then simplify to:

$$\gamma_c = \frac{4\pi\mu^2 n \omega}{ch} \cdot \frac{\Delta W_c}{(\omega - \omega_0)^2 + (\Delta W_c)^2} \qquad (2.20)$$

and

$$\gamma_D = \frac{8\pi^2\mu^2 n \omega}{ch\,\Delta W_D / \sqrt{\pi}} \cdot e^{-\left(\frac{\omega - \omega_0}{\Delta W_D}\right)^2} \qquad (2.21)$$

At optical frequencies, the ratio of either ΔW_D or ΔW_c to ω is an extremely small quantity, so that ω remains nearly constant over the frequency range in which absorption occurs. Hence, equation 2.20 is Lorentzian in form, and equation 2.21 is Gaussian in form.

At resonance,

$$\gamma_c(\omega_0) = \frac{8\pi\mu^2 n\,\omega_0}{ch\,\Delta W_c} \qquad (2.22)$$

and

$$\gamma_D(\omega_0) = \frac{8\pi\mu^2 n\,\omega_0}{ch\,\Delta W_D / \sqrt{\pi}} \qquad (2.23)$$

These lines exhibit different pressure dependencies (see figure 22); at a given temperature, ΔW_D is fixed, while $\Delta W_c = \tau_c^{-1}$. Thus $\gamma_D(\omega_0)$ is a linearly increasing function of pressure, while $\gamma_c(\omega_0)$ is unchanged by variations of pressure*.

_____

*This is because $\gamma_c(\omega_0) \sim n\,\tau_c$. The density of molecules, n, varies directly with pressure, while τ_c varies inversely with pressure. Thus $\gamma_c(\omega_0)$ remains constant. At very high pressures τ_c begins to depart from its inverse pressure dependency and this statement no longer holds.

For pressures intermediate between 10 and 100 millimeters of mercury, the lineshape will be given by an expression somewhere between the limiting cases of equations 2.20 and 2.21. This is shown graphically in figure 2.2.

Saturated case:

In the event that

$$\left(\frac{\mu E}{\hbar \Delta w_c}\right)^2 \gg 1 , \tag{2.24}$$

we cannot ignore the dependence of the absorption coefficient upon E^2. This effect can become sizeable in optical maser spectroscopic techniques, since very high energy densities can be developed.

It can be seen from equations 2.11 and 2.17 that this E^2 dependence has the effect of reducing the net absorption. One can interpret this saturation effect as a result of the fact that when large fields are applied, the molecules cannot make use of all the energy available to them. The rate of radiative transitions increases with field intensity, and as a result the average population of the two interacting levels tends to equalize.

Regardless of whether the absorption is Doppler limited or pressure limited, the saturation parameter, β , is given by

$$\beta = \frac{\mu}{\hbar \Delta w_c} . \tag{2.25}$$

In the pressure limited case the effect of saturation results in additional broadening of the absorption line. Inspection of equation 2.11 reveals that the full width at half-maximum is

$$\Delta w_s = \Delta w_c \sqrt{1 + \beta E^2} . \tag{2.26}$$

$I(\omega)$

I_0

$I_0/2$

$\Delta\omega_c$

$\Delta\omega_c$ HALF WIDTH
COLLISION BROADENED
LINE

$p > 100\ mm\ Hg$

$p < 10\ mm\ Hg$

I_0

$I_0/2$

$\Delta\omega_D$

$\Delta\omega_D$ HALF WIDTH
DOPPLER BROADENED
LINE

ω_0

ω
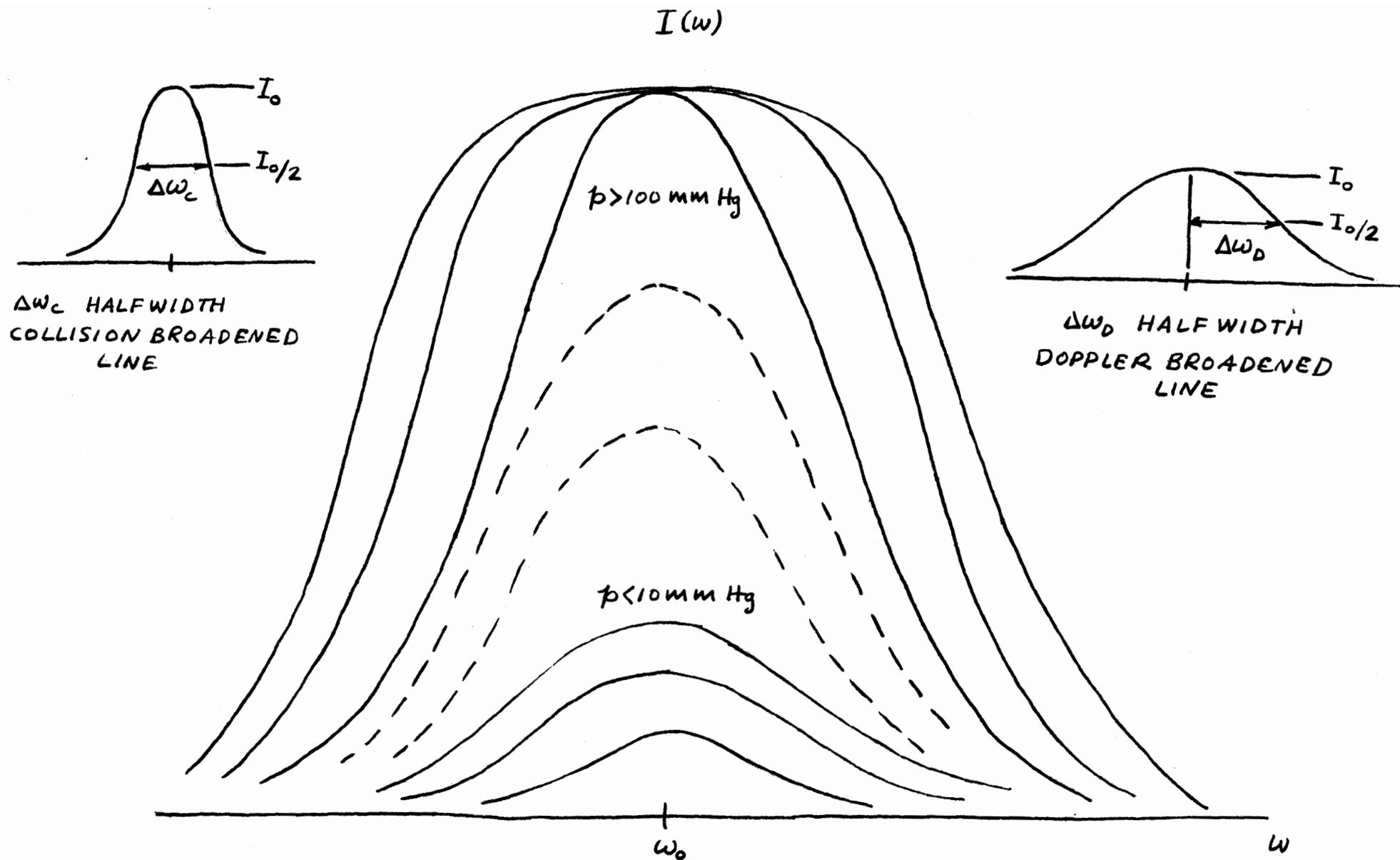
INTENSITY VERSUS FREQUENCY SHOWING
PRESSURE DEPENDENCE

FIGURE 2.2

In the case of the Doppler broadened line, it is seen from equation 2.17 that there is no additional broadening due to saturation.

Further Observations:

(i) The saturation parameter β can lead to information about the matrix element if τ_c is known. Knowledge of τ_c can be obtained from the shape of the collision-broadened line or, alternatively, from information about molecular cross-sections. Data concerning the latter information are not very accurately known at present. It is hoped, however, that experimental determinations of collision-broadened lineshapes may lead to knowledge about β.

(ii) In the case of the Doppler-limited lineshape, the interesting situation exists where χ'' is saturation dependent but χ' is not. Since the phase information is completely contained in χ', this suggests the possibility of making a dispersion measurement of the gas. This dispersion experiment would be unaffected by saturation, and a comparison could be made between the saturation-limited energy absorption and the unsaturated dispersion effects.

(iii) When saturation is negligible, χ' and χ'' obey the well known Kramers-Kronig relations. When the non-linearities of saturation are included, the Kramers-Kronig relations are violated and do not, therefore, hold.

Section 3: Spectroscopy Using An Optical Cavity Resonator.

The spectroscopic technique of containing a gas to be studied in a tuned cavity resonator has been utilized successfully in the microwave region. In the present section the possible application of this technique to the optical region will be discussed.

A suitable experimental arrangement is shown in figure 3.1. The maser beam is incident on one surface of a Fabry-Perot resonator tuneable in the absorption region of the gas in question.   Gas may be admitted into the cavity by means of the inlet value.   The isolator I decouples the maser from the optical cavity.   A suitable isolator utilizing the Faraday effect has been recently constructed in this lab.[6]

Optical Cavity:

Consider an open resonator of the Fabry-Perot type: two identical highly reflecting plane mirrors of area A are rigidly supported parallel to each other and separated by a distance D. If $D \gg A$ the normal modes of the cavity may be treated as plane waves reflecting back and forth between the mirrors. Silvered, dielectric, or other types of reflecting surfaces can be used; in any case, the tangential component of the electric field within the resonator will, for most practical purposes, have a mode at the surface of each mirror. Diffraction losses can be considered small compared with transmission losses.

Power from the maser is coupled into the resonator in the form of an almost monochromatic beams of light impinging up on one mirror. Power is coupled out to the detector by transmission through the other mirror. It is evident that if the surfaces were perfect reflectors no power could be coupled
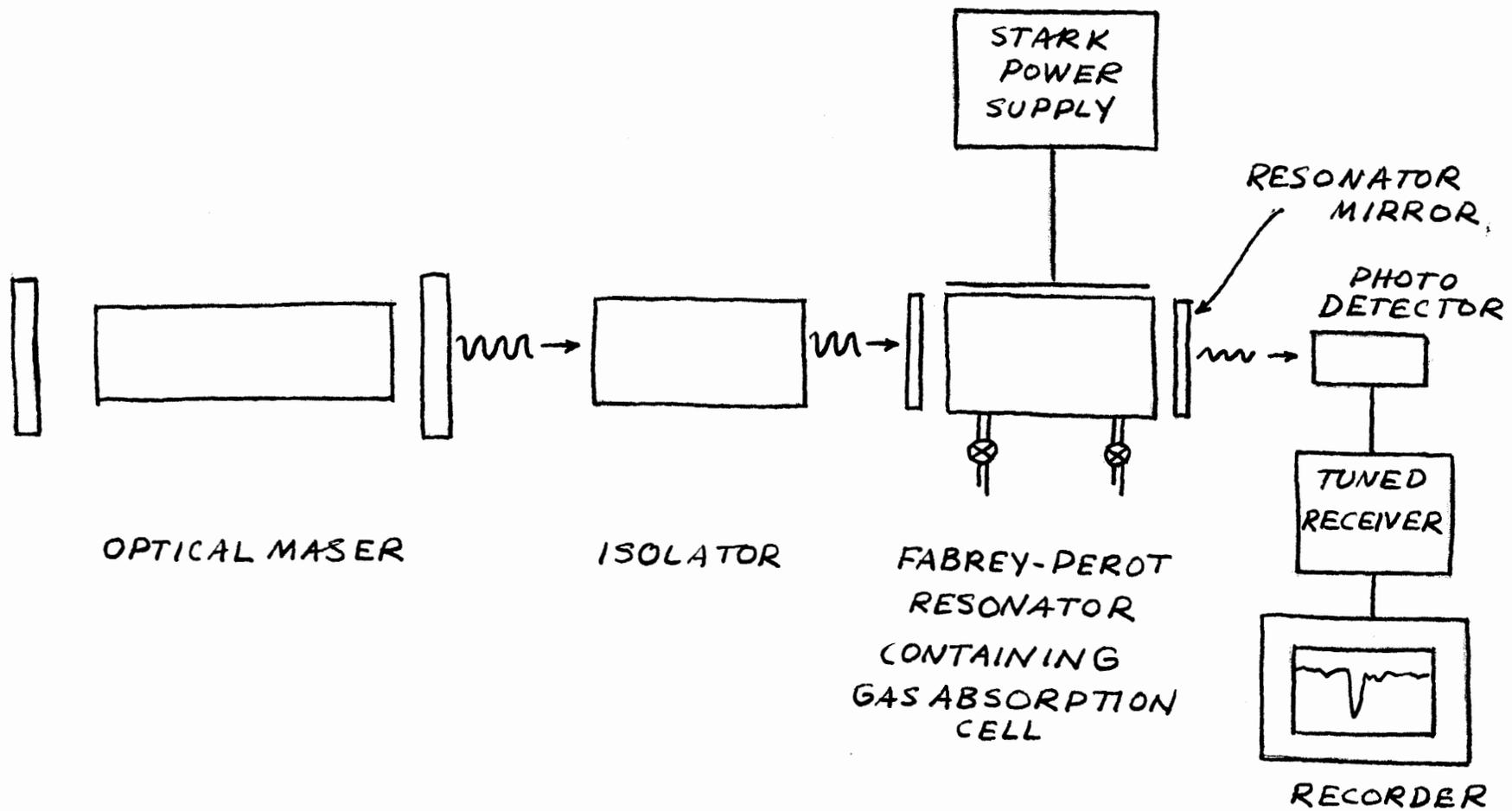
MULTIPLE PASS ABSORPTION EXPERIMENT
UTILIZING AN EXTERNAL RESONATOR

FIGURE 3.1

into or out of the cavity. In practice, mirrors can be made which reflect
as much as 99% of the light incident upon them. Most of the remaining light
will be transmitted through the mirror. A small percentage will be lost
due to scattering and imperfections.

Empty Cavity:

From electromagnetic theory it can be shown that in the case when the
resonator is empty[7]

$$\frac{P_o}{P_i} = \frac{\beta_o \beta_i}{(\omega_o - \omega)^2 + (\beta/2)^2} , \qquad (3.1)$$

where P_i and P_o are, respectively, the power coupled into and coupled out of
the optical cavity,   is the frequency to which the cavity is tuned, and   is
the frequency of the incident radiation; β_i, β_o and β_L are respectively, the
coupling factors for P_i, P_o and the power lost in the cavity, and

$$\beta = \beta_i + \beta_o + \beta_L .$$

Equation (3.1) is a general result and is well known for the microwave
region where, of course, the coupling factors are dependent upon the different
coupling techniques which are employed. In the optical region the coupling
factors, which are characteristics of the mirrors, are given by

$$\beta_i = T_i \frac{c}{2D} ;$$
$$\beta_o = T_o \frac{c}{2D} ; \qquad (3.2)$$
$$\beta_L = L \frac{c}{2D} ;$$

where $\quad T_i = \dfrac{\text{Power transmitted by incident mirror alone}}{\text{Total power}}$

$T_o = \dfrac{\text{Power transmitted by output mirror alone}}{\text{Total power}}$

$$T_2 = \frac{\text{Power loss due to scattering or other sources in the cavity}}{\text{Total power}}$$

(3.3)

and D is the mirror separation. In our case, the mirrors are identical, ie $\beta_i = \beta_o$, and T_L is negligible; thus, equation (3.1) reduces to

$$\frac{P_o}{P_i} = \frac{\beta^2}{4(\omega_o - \omega)^2 + \beta^2} .$$

(3.4)

Filled Cavity:

In the case where the optical resonator is filled with a gas of susceptibility χ, eq. (3.1) is modified:

$$\frac{P_o}{P_i} = \frac{\beta_o \beta_i}{(\omega_o - \omega - 2\pi \chi'_\omega)^2 + (\beta - 4\pi \chi''_\omega)^2}$$

(3.5)

Thus, the saturation effect gives rise to both a frequency dependent power decrease and a "frequency-pulling" off resonance.

Power absorption at resonance:

From equations (3.1) and (3.5), and the standing wave susceptibility relations to be given below, we see that at resonance,

empty cavity $\qquad \frac{P_o}{P_i} \doteq 1$ (3.6)

and

filled cavity $\qquad \frac{P_o}{P_i} \doteq \left(1 - 4\pi \chi'' \frac{\omega}{\beta}\right)^{-2}$ (3.7)

$$\approx 1 + \frac{8\pi \omega}{c} \frac{D}{T} \chi''.$$

By subtracting (3.7) from (3.8) we obtain the interesting result that the change in absorption $\left(\dfrac{\Delta P}{P}\right)_{OC}$ due to the presence of the gas in the cavity is just

$$\left(\frac{\Delta P}{P}\right)_{OC} = -8\pi \frac{\omega}{c} \frac{D}{T} \chi''.$$

(3.8)

Comparing equation (3.8) with equation (2.9), we see that

$$\left(\frac{\Delta P}{P}\right)_{OC} = \left(\frac{\Delta P}{P}\right)_{AC} \cdot \frac{2}{T},$$

(3.9)

where we have written $\left(\dfrac{\Delta P}{P}\right)_{AC}$ for the fractional power loss in the absorption cell. Taking T = 1%, equation 3.11 shows that by utilizing an optical cavity we can obtain increased sensitivity by a factor of 200 over the absorption cell technique of section two. This increased sensitivity enables us to carry out absorption measurements at much smaller pressures than was possible with the absorption cell.

Standing Wave Susceptibility:

The susceptibility given by equations (2.15) and (2.16) holds for a running wave, but is not valid for the case of the standing wave which is set up in the optical cavity of figure 3.1. W. Lamb has calculated the standing wave susceptibility by considering a Doppler broadened atomic line.[8] By expanding the optical maser field in the normal modes of the cavity and treating the inverted population as a quantum mechanical assembly, he obtains the macroscopic polarization. A. Szoke has derrived the same expressions from other considerations[9] which are given in appendix C. In any case, it follows that, in the limit of a Doppler broadened line,

that is, where $\Delta\omega_c \ll \Delta\omega_D$, the susceptibility is given by

$$\frac{\mu^2 n}{\Delta\omega_D}\, e^{-\left(\frac{\omega-\omega_0}{\Delta\omega_D}\right)^2}\left[R-\left(\frac{\mu E}{\hbar}\right)^2\frac{\sqrt{\pi}}{(\Delta\omega_c)^2}\left\{\frac{\Delta\omega_c(\omega-\omega_0)+(\Delta\omega_c)^2\frac{2}{\sqrt{\pi}}R}{(\Delta\omega_c)^2+(\omega-\omega_0)^2}\right\}\right] \tag{3.10}$$

and

$$-\frac{\mu^2 n\sqrt{\pi}}{2\Delta\omega_D}\, e^{-\left(\frac{\omega-\omega_0}{\Delta\omega_D}\right)^2}\left[1-\left(\frac{\mu E}{\hbar}\right)^2\frac{2}{(\Delta\omega_c)^2}\left\{1+\frac{(\Delta\omega_c)^2-\Delta\omega_c(\omega-\omega_0)\frac{2}{\sqrt{\pi}}R}{(\Delta\omega_c)^2+(\omega-\omega_0)^2}\right\}\right] \tag{3.11}$$

in which

$$R=\int_0^{\frac{\omega-\omega_0}{\Delta\omega_D}} e^{-x^2}\,dx \qquad . \tag{3.12}$$

Lineshape

Since

$$\left(\frac{\Delta P}{P}\right)_{oc}\sim\chi'' \tag{3.13}$$

we may determine the absorption lineshape from equation 3.11. It is of interest to study the change in intensity as the absorption line is swept through the maser frequency ω. (figure 3.2) At $\omega=\omega_0$ the coefficient of E^2 is a maximum; therefore, when the maser frequency coincides with the center frequency of the atomic line, the intensity will not be maximum as it is in the traveling-wave case. (compare figures 2.2 and 3.2) In fact, this point will be the center of a relative minimum. This unexpected behavior can be understood by noting that a standing wave can be resolved into two traveling waves of equal intensities but propigating in opposite directions. It is seen from equation 3.11 that the coupling between the electric field and the molecules increases as $\omega-\omega_0$ decreases. For optimum coupling in a traveling wave field, $\omega-\omega_0$ is proportional to the relative velocity of the molecules. Therefore, at $\omega=\omega_0$ (where the relative molecular velocity vanishes for optimum coupling), the molecules couple to both travelling waves with a consequent increase in the overall coupling and therefore the saturation.
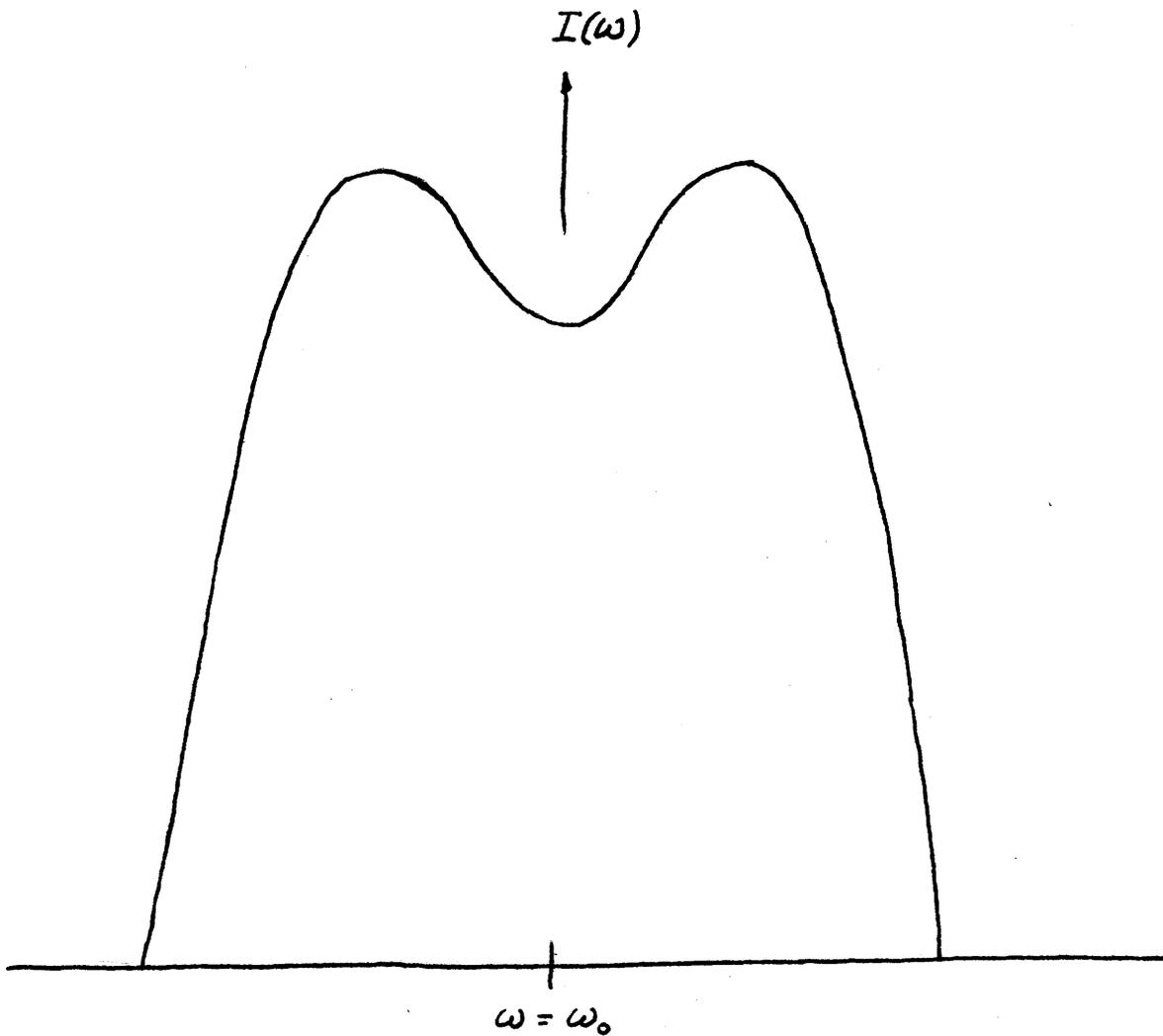
INTENSITY VS OPTICAL MASER FREQUENCY
SHOWING SATURATION EFFECTS FOR A
STANDING WAVE MASER

FIGURE 3.2

Problem of Stability

In the technique suggested in this section the tuning of the optical cavity is critical: sizeable vibration noise is anticipated due to instabilities both in the absorption cavity and in the maser. These instabilities may be due to small temperature variations and other transient effects.

There are a number of ways in which one might compensate for these instabilities. In any event it is of interest to simplify the experimental arrangement. One might consider the possibilities of utilizing a single cavity. Such considerations are carried out in section four.

Section 4: Method Utilizing A Single Optical Cavity

In view of the remarks made at the close of section 3 we are led to examine the possibility of inserting the absorbing gas within the maser cavity. This can be most easily done by increasing the distance between the two mirrors so that the absorbing gas can be included. (See figure 4.)

The solution of the cavity problem is simple in principle, but the actual details are complicated by the fact that the standing wave susceptibility expressions (equations 3.10 and 3.11) are complicated expressions in E and ω, and ω_0. A careful analysis, which will require the aid of a computer, has been planned for the near future. It is worthwhile in the present section to consider some of the qualitative features of the single cavity technique.

Qualitative Operation

Consider the situation when the gas is far away from resonance. This is essentially the same situation as when the gas is not present since the susceptibility of resonance is extremely small. In this situation the maser, suitably adjusted, will oscillate in a normal fashion.

Now let the Stark filled shift the line towards resonance. As ω approaches ω_0 the gas susceptibility, and in particular χ'', increases in magnitude, with a corresponding increase in power loss per unit length. If the maser is close enough to threshold, the absorption will become so large at some $\omega' = (\omega - \omega_0)$ that the condition for oscillation will no longer be met and the maser will cease to oscillate. As the absorption frequency shifts past ω_0, the susceptibility will decrease and finally, when it is sufficiently far away so that the condition for oscillation is restored, the maser will begin to oscillate again.

At the present time techniques are available which enable the helium-neon maser to be set at the threshold of oscillation within one part in 10^4. In this case relative absorptions as low as 10^{-4} (for example, absorption coefficients

STARK
POWER
SUPPLY

ELECTRODE

TUNED
RECEIVER

PHOTO-
DETECTOR
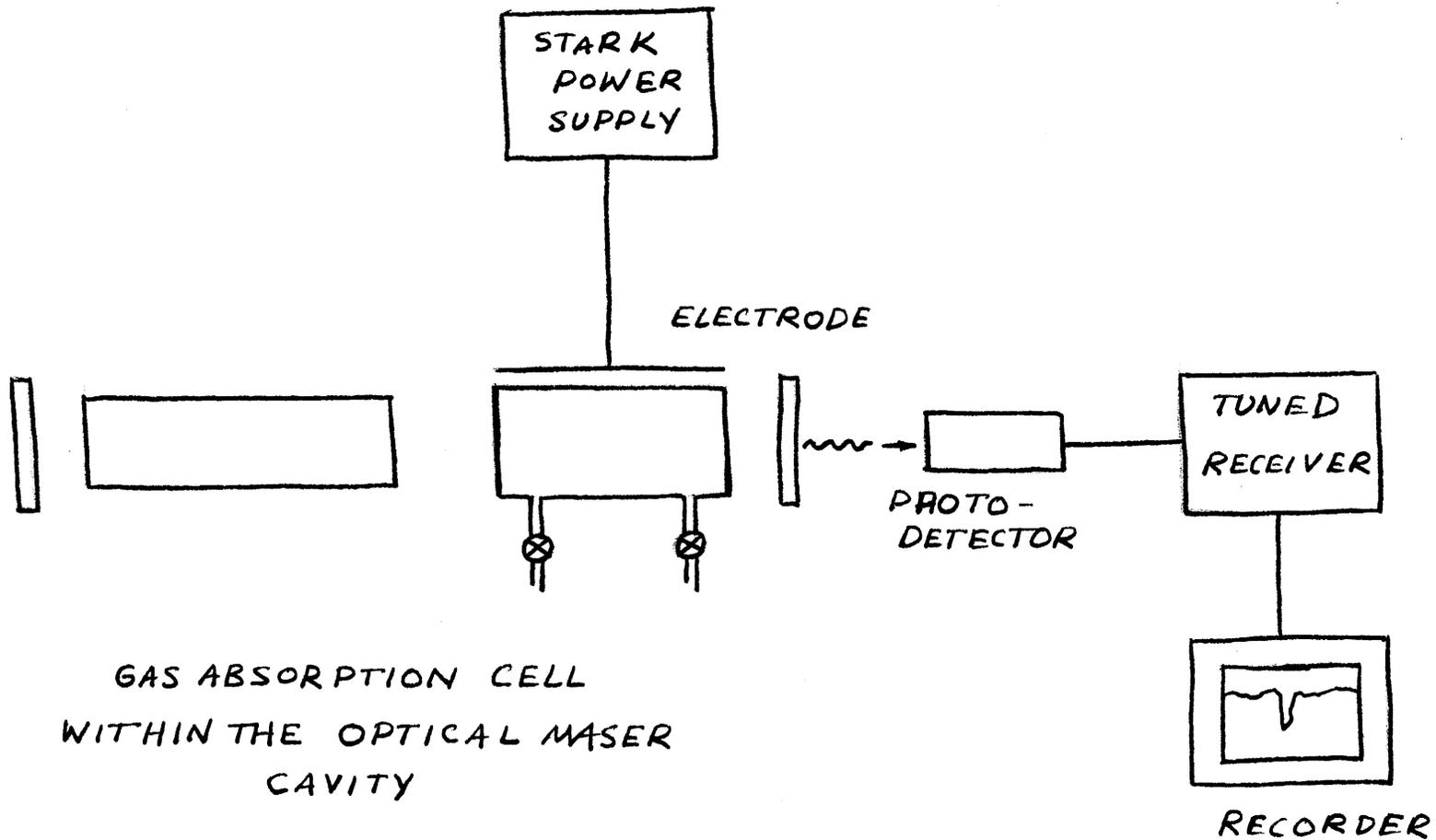
GAS ABSORPTION CELL
WITHIN THE OPTICAL MASER
CAVITY

RECORDER

MULTIPLE PASS ABSORPTION EXPERIMENT
UTILIZING INTENSE OPTICAL FIELDS INSIDE
OPTICAL MASER CAVITY

FIGURE 4.1

of 10^{-4} /meterif a one meter column of gas can be contained in the cavity) would be detectable. This is a sizeable increase in sensitivity and would allow extremely low gas pressures to be utilized. (See section 5).

Experimental Procedure

One possible procedure would be to reset the maser at various levels above threshold. At each setting the gas would be Stark shifted through the desired frequency range, noting the relative frequencies(as a function of Stark voltage) where the maser broke into and out of oscillation. In this way the relative magnitude of the various absorption lines could be ascertained.

Chapter III: Supplementary Techniques

Section 5: Molecular Beam Technique.

It has been noted in Section II that Doppler broadening, which limits
the spectral resolution obtainable at optical frequencies, can be greatly
reduced by employing molecular beam techniques. Such techniques have
long been used in the microwave region.[10] In this section we consider their
possible adaptation to the methods developed in Part II.

The molecular beam technique is based on the fact that the Doppler shift
of a radiating or absorbing molecule depends only upon the component of motion
in the direction of the observer. In the event that the molecule is moving normal
to the direction of observation, there is no Doppler shift. It is therefore of
interest to consider an arrangement in which the maser beam, M, passes through
a beam of molecules, B, such that M and B are perpendicular. Such a molecular
beam can be produced by allowing the gas to enter, through a series of
collimating slits, a region evacuated by continuous pumping (fig. 5.1). Using
such an arrangement, it is possible to reduce the angle of divergence, δ ,
of the beam to the order of 10^{-2} radians. The Doppler shift is thus reduced
by a factor of 100, since

$$\Delta\omega_{mB} \approx \delta \Delta\omega_{0}, \qquad (5.1)$$

where $\Delta\omega_{mB}$ is the Doppler width of the molecular beam. Hence, the Doppler
broadening may be reduced to the order of several megacycles per second,
and if the uncertainty broadening is small, the resolution of the spectral line
may approach the theoretical limit determined by natural broadening.
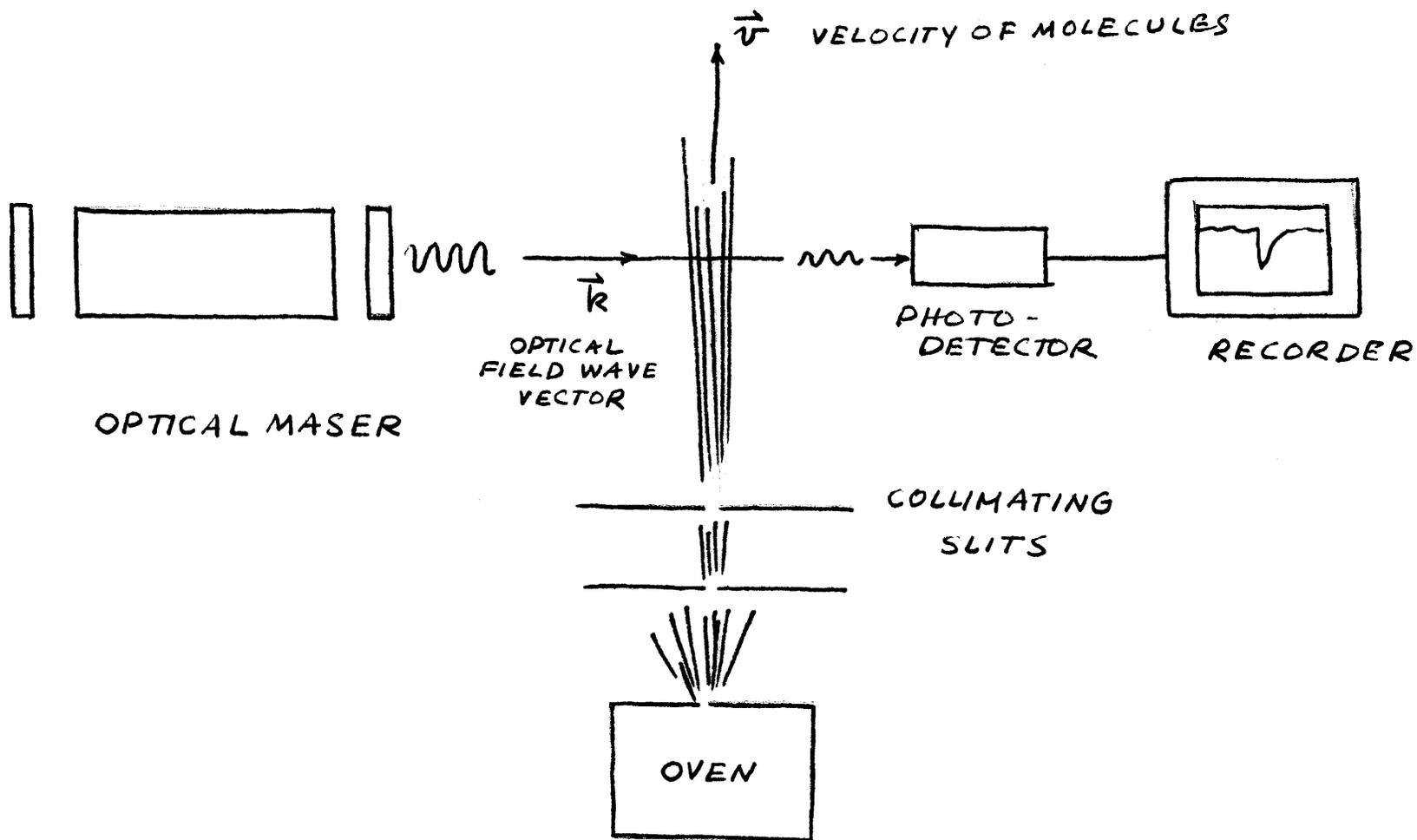
ABSORPTION EXPERIMENT IN WHICH DOPPLER BROADENING IS MINIMIZED, SINCE $\vec{k} \cdot \vec{v} = 0$ FOR THIS ARRANGEMENT

FIGURE 5.1

(It should be noted that in a molecular beam we can assume inter-molecular collisions to be negligible, and therefore $\Delta\omega_{m_{3}} \gg \Delta\omega_{c}$).

The uncertainty broadening is a consequence of the fact that in the experimental arrangement of figure 5.1, the molecule spends only a small time, t_s, in the beam. Since the molecule, in effect, "sees" the beam only during t_s, it may or may not have sufficient time to receive a photon from the maser beam, depending upon whether the fraction t_s/t_n is much larger than, or smaller than, unity. In any case, the broadening due to uncertainty is given by

$$\Delta\nu_u = \frac{1}{2\pi t_s} \cdot \qquad (5.2)$$

In our particular geometry,

$$t_s \approx \frac{d}{\bar{v}} , \qquad (5.3)$$

where $\bar{v}$ is the mean speed of the escaping molecule, and d is the diameter of the maser beam. For the helium-neon maser, d is of the order of several millimeters, hence, at room temperature,

$$t_s \approx 10^{-5} \text{sec.} , \qquad (5.4)$$

which from equation 2.13 is seen to be a full order of magnitude larger than τ_n. In this case, the molecule has ample time to absorb a photon.

We are therefore justified in using the absorption coefficients previously derived[*], where we must now interpret n as n_e , the effective density of molecules within the beam. This number is given by

$$n_e = \frac{d\Gamma}{A\bar{v}}$$ (5.5)

where Γ is the rate at which molecules impinge upon the flat wall in which the slit is located, and A is the area of the slit. The rate Γ is given by kinetic theory[//] to be

$$\Gamma = \frac{1}{4} n \bar{v} A$$ (5.6)

where n is the density of molecules in the oven which is, as in equation 1.11 given by

$$n = 3 \times 10^{16} p.$$ (5.7)

The effective density is therefore given by

$$n_e = \frac{n d}{4}$$ (5.8)

which in our case is of the order of 10^{14} molecules/cm^3. This low density corresponds to 10^{-2} mmHg in the static cases previously considered. We thus expec a very small signal, and the methods of sections 3 and 4 seem most suitable when molecular beam techniques are to be utilized.

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* Although the Doppler width has been reduced, the collision width has been also, and we are still in the limit in which $\dfrac{\Delta \omega_c}{\Delta \omega_D} \ll 1.$

Section 6: The Gallium Arsenide Maser-Diode

The recent development of GaAs maser-diodes[12] suggests the attractive possibility of a tuneable maser source. The frequency of the maser line, which is essentially determined by the energy gap of the semiconductor, is temperature dependent. Typical values of the oscillation frequencies are 8400A^o at liquid nitrogen temperature (77°K) and 9000 A^o at room temperature. The diodes also oscillate at liquid helium temperature.

Because of the tuneability of Ga As no Stark field would be necessary and a very simple spectroscopic technique might be employed. However, the mere fact that GaAs is tuneable by temperature sets an inherent limitation on the stability of the oscillation frequency. Because of this fact it is not at all clear at the present time to what extend GaAs would be of use in extreme high resolution spectroscopy. Experiments involving this tuneable-source technique are planned in this laboratory inthe near future.

Appendix A: Running Wave Susceptibility from Quantum -Mechanical Considerations

Consider the quantum -mechanical system, χ, describing a single molecule which has two states, u_a and u_b, with corresponding energies W_a and W_b, $W_a > W_b$, between which radiative transitions can occur. These transitions may be stimulated by an electromagnetic wave which will be treated as a time dependent penetration on the time-independent system. The Schrödinger equation in this case is

$$\left(H_o + H'(t)\right)\Psi = i\hbar \frac{d\chi}{dt} \qquad (A\bullet 1)$$

where H_o is the unperturbed Hamiltonian of the system and H' is the time dependent perturbation Hamiltonian. The time independent energy eigenfunction of the unperturbed system satisfy

$$H_o u_a = W_a u_a$$
$$H_o u_b = W_b u_b \qquad (A.2)$$

The wave function at any time can by expressed by

$$\Psi = a(t)e^{-i\omega_a t} u_a + b(t)e^{-i\omega_b t} u_b, \qquad (A.3)$$

where $[a(t)]^2$ and $[b(t)]^2$ are the transition probabilities associated with states u_a and u_b, and

$$\left(a(t)\right)^2 + \left(b(t)\right)^2 = 1 \qquad (A.4)$$

and

$$W_a = \hbar \omega_a \qquad (A.5)$$
$$W_b = \hbar \omega_b.$$

The matrix elements of the Hamiltonian are

$$\langle u_i | H_o | u_j \rangle = W_j \delta_{ij} \qquad (A.6)$$

and

$$\langle u_i | H' | u_j \rangle = H'_{ij}. \qquad (A.7)$$

Then by multiplying equation A. 1 by u_i^* and integrating over all space, one obtains

$$\langle u_i | H | \psi \rangle = i\hbar \left\langle u_i \left| \frac{d\psi}{dt} \right. \right\rangle , \tag{A. 8}$$

which, using equations A. 3, A. 6, and A. 7, can be reduced to

$$\dot{a} = -\frac{i}{\hbar} \left(H_{aa'} a + H'_{ab} b \, e^{i(\omega_a - \omega_b)t} \right) \tag{A. 9}$$

and

$$\dot{b} = -\frac{i}{\hbar} \left(H'_{ba} a \, e^{-i(\omega_a - \omega_b)t} + H'_{bb} b \right). \tag{A. 10}$$

Perturbation Hamiltonian

We take

$$H' = -\underline{E} \cdot \underline{\mu} \cos \omega t \tag{A. 11}$$

as the perturbation applied to the system from t_0 to t. Here $\underline{E}$ is the electric field strength and $\underline{\mu}$ the dipole moment. Then

$$H_{ij} = -E \frac{\mu}{2} \left(e^{i\omega t} + e^{-i\omega t} \right) \tag{A. 12}$$

where

and

$$\mu_{ij} = \langle u_i | \mu | u_j \rangle$$

$$\mu_{ab} = \mu_{ba} = \mu$$
$$\mu_{aa} = \mu_{bb} = 0 \tag{A. 13}$$

since μ is the average of the dipole matrix element along the direction of E connecting the two states.

Calculation of $\bar{P}$

The dipolemoment of the molecule at a time t can be written

as

$$P = \langle \chi | \underline{\mu} | \chi \rangle = b^* a \underline{\mu} e^{i\omega t} + a^* b \underline{\mu} e^{-i\omega_0 t}$$

(A. 2

Hence

$$P = \frac{\varepsilon}{\hbar \omega} e^{i\omega t} \left\{ \frac{i}{2} \sin \Omega (t-t_0) + \left(\frac{\omega - \omega_0}{\Omega} \right) \sin^2 \frac{\Omega}{2} (t-t_0) \right.$$

$$+ \text{complex conjugate}$$ (A. 2

If we have an assembly of molecules, we can relate the average dipole moment

$\bar{P}$ of a single molecule with the polarization P:

$$P = \frac{\text{number of dipoles}}{\text{unit volume}} \; \bar{P} \; .$$ (A. 25)

As is discussed in section1, the molecules are in constant collision with one

another. In calculating $\bar{P}$ we must therefore take into consideration the fact

that a molecule can, on the average, interact with the field only for a mean time

$\hat{\tau}_c$ without being disturbed by a collision. We assume these collisions to be

"hard"; that is, after undergoing a single collision the molecule loses all

"memory" of past collisions, and the phase relatio nship between the field

interactions before and after a collision is random. The normalized distribution

function of the time $t- t_0$ since the last collision is given by equation 1.9:

$$f(t_0) dt_0 = \frac{1}{\tau} e^{-(t-t_0)/\tau} dt_0 \; .$$ (A. 26)

The dipole moment must therefore be averaged over all possible times since the

last collision occured:

$$\bar{P} = \int_{t_0 = -\infty}^{t_0 = t} f(t_0) p(t_0) \, dt_0.$$ (A. 27)

Performing the integration, we obtain

$$\bar{P} = \frac{\mu^2}{\hbar \left[\Omega^2 + (1/T_c)^2\right]} E e^{i\omega t} \left[i\gamma + (\omega - \omega_0)\right] + \text{complex conjugate}$$

(A. 28)

Calculation of χ

Using equation A. 25 and taking n as the molecular density it follows that

$$P = \frac{\mu^2 n}{\hbar \left[\Omega^2 + (\frac{1}{T_c})^2\right]} E e^{i\omega t} \left[i\gamma + (\omega - \omega_0)\right] + \text{complex conjugate}$$

(A. 29)

Finally, noting that

$$\mathcal{E} = \mathcal{E} \cos \omega t = \frac{1}{2} \left\{ \mathcal{E} e^{i\omega t} + \mathcal{E}^* e^{-i\omega t} \right\}$$

(A. 30)

and remembering from equation 2. 2 that

$$P = \chi E$$

(A. 31)

we obtain

$$\chi = \frac{n \mu^2}{\hbar} \left\{ \frac{(\omega - \omega_0) - i \Delta \omega_c}{(\omega - \omega_0)^2 + (\Delta \omega_0)^2 + (\frac{E \mu}{\hbar})^2} \right\}$$

(A. 32)

which is recognized to be equation 2. 10 in the text.

Appendix B: Molecular Density of the Lower State of a Transition

The quantity n which appears in equation 2.10 and subsequent equations can be written

$$n = N f \qquad (B.1)$$

where N is the molecular density of the gas in the absorption cell and f is the fraction of these molecules in the lower of the two states involved in the transition. The exact value of f is given by [13]

$$= e^{-\nu \frac{h\omega_e}{kT}} \left(1 - e^{\frac{h\omega_e}{kT}}\right) (2J+1) \frac{hB}{kT} e^{-\frac{hBJ(J+1)}{kT}} \qquad (B.2)$$

where we have considered the possibilities of transitions from rotational and vibrational levels. At room temperature the following approximations can be made:

$$\frac{h\omega_e}{kT} \approx 50 \qquad (B.3)$$

$$\frac{hB}{kT} \approx \frac{1}{200} \qquad (B.4)$$

Also, in the optical region the energy gap between levels is large. The relative population of the upper and lower states is given by

$$\frac{n_u}{n_e} = e^{-h\nu/kT} \qquad (B.5)$$

where we have written n_u and n_e for the relative numbers in the upper and lower states respectively. We therefore note that essentially all the molecules are in the lower state.

Inserting (B.3) and (B.4) into (B.2), and bearing in mind (B.5), B.2 reduces to

$$f \doteq e^{-\nu \frac{h\omega_e}{kT}} (2J+1) \frac{hB}{kT} \qquad (B.6)$$

which is of the order of $1/200$ for $\nu = 0$ and vanishes for all other ν.

We may thus conclude that an order of magnitude of n yields

$$n \approx \frac{N}{200}. \qquad (B.7)$$

Appendix C: Simplified Derivation of Standing Wave Absorption*

Consider a gas contained in an optical cavity in which a standing wave is propagating. This standing wave may be resolved into two running waves of equal intensity but propagating in opposite directions. The absorption cross-section of a single molecule in a running-wave field characterised by frequency ν can be written

$$\sigma(\omega, k > 0) = \frac{\sigma_0 \, (\Delta\omega_c)^2}{[\omega - \omega_0(1 - \tfrac{v}{c})]^2 + (\Delta\omega_c)^2} \qquad (C.1)$$

where the constant factors have been absorbed into σ_0, V is the velocity of the molecule, and the other symbols are consistent with the text.

The total absorption I by the gas, except for a proportionality factor, may be written

$$I \sim \int_{-\infty}^{\infty} n(v)\big[\sigma(k,v) + \sigma(-k,v)\big] E^2 \, dv \qquad (C.2)$$

where $n(v)$ is the excess population in the lower state as a function of the molecula velocity. If the applied electric field is small, then $n(v)$ will just be the Maxwellian velocity distribution of equation 1.14a.

$$n_0(v) = \frac{N}{u\sqrt{\pi}} e^{-v^2/u^2} \qquad . \qquad (C.3)$$

To take the saturation into account we must solve a rate equation (Boltzmann equation) for the population:

$$\frac{1}{2}\frac{dn(v)}{dt} = \frac{1}{2}\frac{dn(v)}{dt}\bigg/_{collision} + \frac{n(v)}{\tau_n} \qquad (C.$$

* We shall here calculate only the absorption which corresponds to χ''; it is also possible to calculate χ' on this basis.

where $\frac{d n^{(v)}}{dt}\big/_{coll.}$ is the depopulation of the state due to collisions, and τ_n is the natural lifetime of the state. Assuming that the saturation is small,

$$\frac{dn(v)}{dt}\bigg/_{coll} \approx \frac{d n_0(v)}{dt}\bigg/_{coll}, \qquad (C.5)$$

and therefore this term can be eliminated by considering the case with no electric field; that is, the steady state:

$$\frac{n_0(v)}{\tau_n} = -\frac{d n_0(v)}{dt}\bigg/_{collision}. \qquad (C.6)$$

The steady state solution of the rate equation C.4 is

$$n(v) \approx -N_0(v)\,\frac{1}{1 + \tau_n E^2 [\sigma(k,v) + \sigma(-k,v)]}$$

$$\approx -n_0(v)(1 - \tau_n E^2 [\sigma(k,v) + \sigma(-k,v)]) \qquad (C.7)$$

where we have made the assumption that the second term in the denominator is small.

Also from equation 2.9,

$$\Delta I = -4\pi \frac{\omega}{c} \chi'' I L \qquad (C.8)$$

where ΔI is the intensity gain in length L.

Solving equation C.8 for χ'', substituting equations C.2 and C.7, and finally integrating over velocity, we obtain

$$= -\frac{u^2 n\sqrt{\pi}}{2\Delta\omega_0}e^{-\left(\frac{\omega-\omega_0}{\Delta\omega_0}\right)^2}\left[1 - \left(\frac{uE}{\hbar}\right)^2 \frac{2}{(\Delta\omega_0)^2}\left\{\frac{1 + (\Delta\omega_c)^2 - \Delta\omega_c(\omega-\omega_0)\frac{2}{\sqrt{\pi}}R}{(\Delta\omega_c)^2 + (\omega-\omega_0)^2}\right\}\right] \qquad (C.9)$$

which is just equation 3.11.

FOOTNOTES:PART II

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