SEMIANNUAL STATUS REPORT

The Ohio State University

ElectroScience Laboratory

(formerly Antenna Laboratory)
Department of Electrical Engineering
Columbus, Ohio 43212

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Sponsor	National Aeronautics and Space Administration Office of Grants and Research Contracts Washington, D. C. 20546
Grant Number	NsG-74-60
Investigation of	Receiver Techniques and Detectors for Use at Millimeter and Submillimeter Wave Lengths
Subject of Report	Semiannual Status Report
Submitted by	The Ohio State University ElectroScience Laboratory Department of Electrical Engineering
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SEMIANNUAL STATUS REPORT

I. INTRODUCTION

The research activity during the past period has been concentrated in the following areas: (a) determination of the exact molecular force constants of CO_2 molecule. (b) solution of the second order coupled linear differential equation which arises from the calculation of excitation cross section of co_2. (c) experimental work on investigation of infrared lasers. Parts (a) and (b) arose from earlier calculations to determine cross section for excitation or de-excitation of a molecular vibrational state through collision with an incoming structure less particle such as a Helium atom. In these calculation we have taken into consideration the fact that the vibrational states of the CO_2 molecule are not pure independent states but are rather mixed. This is due to the non linearities in the vibrational Hamiltonian of the CO_2 molecule. This consideration forces one to first determine the exact eigen states of the CO_2 molecule. For this purpose we have had to diagonalize matrices up to 48 by 48. Of course to do so one should have the correct set of force constants. This problem is discussed in Section A of this report. More over this consideration complicates the problem a little more. In Section B of this report we discuss the problem of solving the resulting equations for the calculation of the excitation cross section.

A. Calculations of the Vibrational Wave Functions

The vibrational Hamiltonian for CO_2 molecule is given by[1]

$$
\begin{aligned}
(1)\qquad H = {} & \frac{2\pi^2 c}{h}\left[\omega_1 p_\sigma^2 + \omega_2\ (p_\xi^2 + p_\eta^2) + \omega_3 p_\zeta^2\right] \\
& + \frac{1}{2} hc\ (\omega_1 \sigma^2 + \omega_2 \rho^2 + \omega_3 \zeta^2) + hc\ (a\sigma^3 + b\sigma\rho^2 + c\sigma\zeta^2) \\
& + hc\ (d\sigma^4 + e\rho^4 + f\zeta^4 + g\sigma^2\rho^2 + h\sigma^2\zeta^2 + i\rho^2\zeta^2)
\end{aligned}
$$

where a, b, . . . i are the molecular force constants. Because of Fermi resonance the vibrational states of the CO_2 molecule are mixed. The constants a, b, . . . i determine the degree of the mixing. In order to find the exact wave function which are to be used in the calculations of excitation cross section one must first determine the constants a, b, . . . i. This can be done approximately by an iterative process, that is to say first a set of constants a_o, b_o. . . are substituted into the Hamiltonian and a matrix $[A_o]$ is found such that $[A_o]^{-1} H(a_o, b_o \ldots) [A_o] = [E]$ where $[E]$ is a diagonal matrix. Then instead of E one substitutes the experimental energy value $[E_o]$ and the linear set of equations

$$[A]^{-1} H(a_1, b_1 \ldots) [A] = [E_o]$$

are solved for $a_1, b_1, \ldots$. This process is continued until the set $a_i, b_i \ldots$, when substituted in H and diagonalized, gives the best fit with the experimental values. For this propose 48 states were chosen and this amounted to solving matrix equation of order 48 by 48. However it must be noticed that this iterative linearization of a nonlinear equation does not converge but rather oscillates when the off diagonal elements connecting two eigen states are large compared to the difference of their eigen values. In that case one chooses that set of constants which gives the best fit of energies to the experimentally found values.

B. Calculation of the Excitation Cross Section

In solving the problem of excitation cross section through collision one can use the method of partial waves. This leads to a set of n second-order coupled differential equations of the form

$$(2) \quad \left[\frac{d^2}{dr^2} + k_n^2 - \frac{\ell(\ell+1)}{r^2}\right] F_n^{\ell}(r) = \sum_{e'm'} V_{n m'}(r) F_{m'}^{\ell'}$$

where

$$(3) \quad V_{n m'} = V_o C_{n m} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

and V_o and $C_{n m}$ are constant coupling coefficients. This second order coupled set of equations is however not regular since the coefficient of the independent variables F_m^{ℓ} have singularities of order 12. We seek here those solutions of $F_n^{\ell}(r)$ which for large r behave as $F_n^{\ell} e^{ikr}/r$. For a given dimension N, because of the coupling, each wave function F_n^{ℓ} has 2N independent solutions, and one must choose a linear combination of these solutions which behave as $F_n^{\ell} e^{ikr}/r$. The excitation cross section is proportional to $|F_n^{\ell}|^2$. The above set of equations has been programed on the computer. The coefficients $V_{n m}$ have been calculated and the differential equations have, after much programing been solved for low value of ℓ.

C. The Experimental Work

The experimental work has been directed towards finding new laser lines in hydrocarbons by burning them in a discharge with oxygen: but so far all the strong laser lines which have been found seem to belong to the various vibrational lines of CO and the P and R branches of the (0.001)-(100) line of the CO_2 molecule. These radiations lie about the 5 μ line which is that of CO molecule and 9.6 or 10.6 μ of CO_2. A number of other gases have been tried. In particular we shall mention here the combination of Frion and Helium. Two different species of the Frion gas has been used in a discharge with helium. A number of lines have been observed, some belonging to the He transitions but the others have not been yet identified. The helium transitions seen to be intensified when the Frion gas is added to the discharge. If such is the case then the Frion must help depopulating the lower level of the helium transition-line. For investigating this possibility we are now calculating the life times of all the states of helium which are involved, so as to compare them with the collision times. The laser has the internal mirror geometry and the mirrors are gold coated.

II. PROGRAM FOR PERIOD
APRIL 1967 THROUGH SEPTEMBER 1967

For the coming period we plan to finish the excitation calculations concerning the CO_2 molecule and continue the experimental work, but using pulsed currents of very short duration.

III. PROPOSED FUTURE PROGRAM
OCTOBER 1967 TO SEPTEMBER 1968

A. Introduction

For the coming year, we are interested to continue our calculation of the effect of the collision of simple gases with CO_2 molecule. It has been shown[1] that, when in a CO_2 discharge, Foreign gases such as N_2, He, H_2O or H_2 are introduced, the life time of certain vibrational levels change drastically. This in turn could effect the distribution of the emanated infrared intensities. The purpose of this work is to study theoretically the excitation or rather de-excitation cross section of some of the CO_2 vibrational levels by collision. This problem can be illustrated by the following simple example. Imagine as in Fig. 1, that two vibrational levels are radiatively connected.

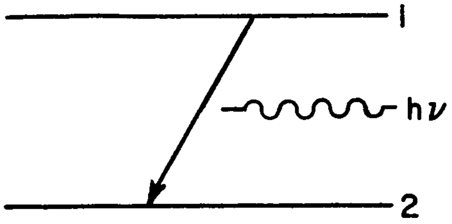

Fig. 1.

If in an electric discharge level (1) gets more populated than level (2), then one would observe a radiation hν of an intensity which is porportional to the difference of the population of the levels (1) and (2). In other words neglecting the degeneracies of the levels one could write for the intensity I

(4) $I \propto (N_1 - N_2)$

The steady state intensity I depends on the difference in population of levels (1) and (2). But

(5) $$\frac{dN_1}{dt} = -\frac{N_1}{\tau_1} + R_1 \ , \quad \frac{dN_2}{dt} = -\frac{N_2}{\tau_2} + R_2$$

where τ_1, τ_2 are the effective life times of levels (1) and (2) due to collision or radiative decay while R_1 and R_2 are the total excitation rates due to cascading effect or any other means. In a steady state we have $dN_i/dt = 0$, $i = 1, 2$ or

(6) $N_1 = \tau_1 R_1 \ , \ N_2 = \tau_2 R_2$

and hence

(7) $I \propto (\tau_1 R_1 - \tau_2 R_2)$

If in the steady state situation $\tau_2 R_2$ becomes larger than $\tau_1 R_1$ then no radiation will be observed from the discharge. Rather the gas would be obsorbtive to the radiation corresponding to the difference of the levels. However, if in our discharge we introduce a foreign gas which would prefentially through collision depopulate level 2, this would effectively decrease the life time τ_2 and hence the product $\tau_2 R_2$ will be decreased and the observed result would be an increase in the intensity I, or decrease in absorption.

This we know is possible[1], since different modes of vibration, or in other words the way the atoms of a molecule move with respect to each other in a given molecular mode could make a difference when colliding with another particle. In other words the cross section for giving up energy would not be the same for each mode or its harmonic. The direct effect of a foreigh gas on levels one and two is through transfer of vibrational energy to kinetic energy by collision or by resonance exchange if the two colliding particles have resonant energy levels within the kT energy limit.

B. Method of Calculation

When a vibrationally excited molecule, within a discharge tube makes collision with another molecule or atom, depending upon the temperature of the gas, the vibrational energy of the first molecule can be transfered to the kinetic energy of the second molecue or atom. However, if the second molecule has a vibrational energy or a harmonic of that energy close to that of the vibrational energy of the first, then it is possible for the first molecule to vibrationally excite the second molecule. It is the purpose of this work to calculate the cross section for the transfer of vibrational energy from one simple molecule to the kinetic or vibrational energy of another simple molecule. In particular we are interested in the interaction of CO_2 molecule with other molecules such as H_1, H_e, N_2 and CO_2. In works available,[3] on the calculation of the excitation cross section of vibrational to kinetic energy transfer of CO_2 performed by other researchers it has mostly been assumed for the sake of simplification that the vibrational levels of the CO_2 molecule are pure states and calculations have been done with this assumption in mind. However, due to the anharmonicity of the potential function and the existance of the Fermi-resonances between the various vibrational levels, the states do not remain pure, but are rather mixed. This consideration can give different results for the cross sections. The Hamiltonian for the CO_2 molecule, up to the quartic anharmonic terms has been given[2] and the force constants are fairly accurately determined. For this reason one can determine the degree of the mixing of the wave functions. Already we have diagonalized matrices up to 48 by 48 using force constants given by Denison (1940)[2] and also force constants calculated from more recent observations. The Hamiltonian for the CO_2 molecule is given by

$$(8) \quad H_{vib}(CO_2) = \frac{2\pi^2 c}{h}\left[\omega_1 p_\sigma^2 + \omega_2 (p_\xi^2 + p_\eta^2) + \omega_3 p_\zeta^2\right]$$

$$+ \frac{1}{2} hc\,(\omega_1\sigma^2 + \omega_2\rho^2 + \omega_3\zeta^2) + hc\,)a\sigma^3 + b\sigma\rho^2 + c\sigma\zeta^2)$$

$$+ hc\,(d\sigma^4 + e\rho^4 + f\zeta^4 + g\sigma^2\rho^2\zeta^2 + i\rho^2\zeta^2)\,.$$

where ξ, σ, η and ζ are the normal coordinates given by the following relations

$$(9) \quad \sigma = 2\pi\,(\omega_1\, mc/2h)^{\frac{1}{2}} q \qquad \eta = 2\pi(\omega_2\,\mu c/h)^{\frac{1}{2}}\zeta\ , \quad \rho^2 = \xi^2 + \eta^2$$

$$\xi = 2\pi\,(\omega_2\,\mu\, c/h)^{\frac{1}{2}} x \qquad \zeta = 2\pi\,(\omega_3\mu\, c/h)^{\frac{1}{2}}$$

m is the mass of oxygen and $\mu = 2mM/2m+M$ is the reduced mass with M the mass of carbon,q measures the change in distance between the two oxygen atoms and x, y, z are the coordinates of the carbon atom with respect to the center of gravity of the two oxygen atoms, with the z axis oriented along q. Finally, a, b, c... etc. are the anharmonic force constants. When the CO_2 molecule makes a collision with another atom or molecule such that there is a transfer of energy between the vibrational energy of CO_2 and the kinetic energy of the colliding particle, the Hamiltonian for such a process is written in the following form

$$(10) \quad = H_{vib}(\sigma\,\rho\,\zeta) + H_{interaction}(r, \sigma, \rho, \zeta) + H_{kinetic}(r)$$

where $H_{kinetic}$ is simply the kinetic energy of the incoming particle compared to a frame of reference in which CO_2 is at rest. The interaction potential is however not easily determinable, but can be approximately written in the form of

$$(11) \quad V_{int.} = V(r)\,V(\sigma)\,V(\rho)\,V(\zeta)$$

where it has been assumed that the potential is seperable. However it should be kept in mind that this is an approximation. $V(r)$ is usually taken to be a Leonard-Jones potential and for ease of calculation and because of the short range effect of the interaction potentials $V(\sigma)$, $V(\rho)$, or $V(\zeta)$ are assumed to have an expontential form of the type $e^{-A\sigma}$ where A is determined usually by matching the expontential to a Leonard Jones potential at the point of the classical nearest approach.

When there is a vibrational exchange of energy between two molecules another term has to be added to the Hamiltonian of Eq. (10) which corresponds to the vibrations of the second molecule and moreover the interaction potential has to be modified. Some detailed work on this subject has been given by Takayanagi[4] with an extensive bibliography.[5]

C. Experimental Work

As far as the experimental work is concerned we would like to continue work along the same line of investigation that we have followed namely the finding of coherent sources in the far infrared region of the spectrum. During the past periods, we have mixed air with hydrocarbon, and other molecular gases of interest. When the correct proportions of the gases were passed through a discharge tube we were able to burn the gases and produce CO_2 and CO and other compounds, which gave strong laser lines. These lines were determined mostly to be due to CO and CO_2. In this investigation we were however interested in longer wave length transitions due to other by products rather than CO and CO_2. Since long chained, or complex hydrocarbons have many vibrational levels, upon colliding and chemically joining with oxygen i. e. burning the by products could possibly become excited and if produced with sufficient efficiency one may have population inversion and hence laser action. However, the continueous discharge with which we operated our laser, gave almost complete burning of the hydrocarbon and the only by products present were CO and CO_2.

We are planning however to use the same compounds, but instead of continueous discharge to pulse the gas mixture with high current short duration pulses. Because of the intensity of current and its short duration it may be possible at this time to produce other by products besides CO and CO_2, and these chemically formed by products may be vibrationally excited.

IV. SUMMARY

It is intended to continue research on the excitation cross section calculations for CO_2 and He by changing the interaction potential and finding its effect on the cross section of the vibrational levels of CO_2. Moreover we like to calcualte the effect of some other particles besides helium such as H_2O, H_2, CO and etc. on CO_2. The second step in this work would be the calculations of resonant exchange of energy between vibrational levels of CO_2 and other molecules with which CO_2 may have a resonant energy level.

REFERENCES

1. Weber, M. J. and Deutsch, T. F., J. of Q. E.

2. Dennison, D. M., Rev. of Modern Phys. Vol. 12, No. 3, p. 175 (1940)

3. Marriott, R., Proc. Phys Soc., Vol. 86, p. 1041, (1965)

4. Takayanagi, K., Supp. of Progress of Theoretical Phys. No. 25, (1933)

5. Takayanagi, K., Science Rep. of Saiten Univ., Vol. V., No. 1, p. 14, (1965)