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## VIBRATIONAL RELAXATION PROCESSES IN $CO_2$-$N_2$-$H_2O$ LASER SYSTEMS

by

Yan Haixing

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# VIBRATIONAL RELAXATION PROCESSES IN $CO_2$-$N_2$-$H_2O$ LASER SYSTEMS

Yan Haixing

SUMMARY: This article discusses a number of important questions concerning relaxation processes: the *V-V* energy transfer mechanism inside $\overset{\Pi\Pi}{CO_2^*(\nu_3)}$ molecules; the mechanisms involved in the main reactions of water on relaxation processes; resonant energy transfer between $\overset{NU}{\nu_1}$ and $\overset{NU}{\nu_2}$ in $CO_2$ ; similarities and differences in the relaxation rates for expansion and compression flows; and, possibilities of non-equilibrium existing between different levels of rotational energy and between different levels of vibrational energy within the same vibrational mode. The article points out that it is necessary to do more detailed research on these questions. The content of these discussions is also appropriate for use with other gas laser systems. Chinese Language, [illegible] ←

This article is a continuation of reference [1], and mainly carries out an analysis of several important questions relating to relaxation processes in this laser system.

## I. THE RELAXATION MECHANISM IN $CO_2^*(\nu_3)$ CONSUMING LASER PRODUCTION

The great majority of relaxation experiments are only able to obtain measurements of the speed of energy transfer from $CO_2(\nu_3)$ to the $\nu_1$ and $\nu_2$ composite vibrational mode (recognizing that the latter is in local equilibrium). Moreover, they are not able to precisely determine the end state of the reaction.

At the present time, the precise relaxation mechanism, except for methods involving a small number of experiments, is still mainly dependent on theoretical analysis.

From theoretical analysis, it is possible to know that the energy differential $\Delta E$ in the *V-V* process (furnished or taken from level movement) is reduced. The relaxation speed is rapidly increased. In the process, the overall quantum number is increased. And, the speed will take an abrupt drop [2].

Moore and others took the dependence relationships obtained from experiments or the speeds of different systems (such as mixtures of gases with various types of inertias) and made comparisons with the reduced mass relationships and the results of theoretical calculations. They worked backward to deduce possible mechanisms of relaxation [3]. It is recognized that $\Delta E$ should be in the range 200-300 $cm^{-1}$ , and that $CO_2(11^10)$ is the main final state. Kamimoto and others [4] as well as Sato and others [I:69] also tried handling the problem with wave excitation tube results for different relaxation mechanisms.

Optical-acoustic laws make it possible to empirically make a precise description of the $G$ factor for relaxation mechanisms (V-V (vibration energy ratio between the final reaction state in the process and the initial state). As far as $CO_2$, is concerned, the $G$ value is as shown in Table 1. For a series of work done by Huetz-Aubert and others [I:39;5,6]* the results are shown in Table 2. The lack of data for He in Table 2 is due to the similarities in experimental data for sensitivites to $G$, which lead to an inability to determine values for $G$. It can be seen that different relaxation mechanisms accompanying collisons can be different. For inertial or noble gases, $G$ seems to increase with increases in mass. As far as double atom or multiple atom molecules are concerned, there are no simple regularities. Slobodskaya [7], at room temperature, determined $G$ for $CO_2$ to be 0.9. Cannemeijer and others [I:31,40;8] determined that, for pure $CO_2$, the final state is $3\nu_2$, . When noble gases accompany the collisions, it is $2\nu_2$, . When $N_2$ accompanies them, the final state is $1 \sim 3\nu_2$, . These results are not clearly separable.

In summary, up to the present time, research concerning the mechanism of laser output dissipation in $CO_2^*(\nu_3)$ has not been adequate. Differing accompaniments to the collisions even exist to the extent that, within different ranges of temperature, it is possible to have different relaxation mechanisms. Under conditions at the present time, we choose $11^10$ to be the reaction's final state. This is due to the fact that $11^10$ and $00^01$ have energies which are different by 272 $cm^{-1}$. This is small when compared to the 416$cm^{-1}$ for $03^10$ and $00^01$. Moreover, the overall quantum number or total quantum point for transition is low. This is also supported by theoretical calculations [I:21] and the results of a number of experiments

(1) 表1 $CO_2$分子的G因子

| (2) 反应终态 | $20^{0}0$ | $12^{2}0$ | $12^{0}0$ | $04^{2}0$ | $04^{0}0$ | $00^{0}1$ | $11^{1}0$ | $03^{1}0$ | $10^{0}0$ | $02^{2}0$ | $02^{0}0$ | $01^{1}0$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (3) 能级(厘米$^{-1}$) | 2804 | 2761 | 2680 | 2591 | 2578 | 2349 | 2077 | 1933 | 1388 | 1336 | 1286 | 667 |
| $G$ | 1.194 | 1.175 | 1.141 | 1.108 | 1.097 | — | 0.884 | 0.823 | 0.591 | 0.569 | 0.547 | 0.284 |

1. Table 1 G Factors for $CO_2$ Molecules 2. Reaction Final State 3. Energy Level (Cm$^{-1}$)

(1) 表2 光声法测得的$CO_2$及其混合物的G因子

| (2) 碰撞伴侣 | He | Ne | $N_2$ | Ar | $CO_2$ | Kr | Xe |
|---|---|---|---|---|---|---|---|
| (3) 分子量 | 4 | 20 | 28 | 40 | 44 | 83.7 | 131.3 |
| $G$ | — | 0.54±0.03 | 1 | 0.60±0.01 | 0.80±0.01 | 0.68±0.01 | 0.85±0.01 |

1. Table 2 $CO_2$ Measured by Optical Acoustic Law and G Factors for the Compounds 2. Collision Accompaniment 3. Molecular Weight

## II. THE MAIN EFFECTS OF WATER ON THE RELAXATION PROCESS

People very early turned their attention to the fact that minute amounts of water will have large effects on the relaxation process. In $CO_2$ lasers, a small amount of water greatly increases the speed of the dissipation of laser output to lower energy levels of laser light. Therefore, this obviously increases the gain [I:21]. Water, besides being capable of acting as a collision accompaniment to dissipate the laser or excitation output of $CO_2^*(\nu_2)$、$CO_2^*(\nu_3)$ and $N_2^*$ can make it possible for V-V exchanges to exist between molecules; for example,

$$CO_2^*(\nu_2)+H_2O$$
$$\rightleftharpoons CO_2+H_2O^*(\nu_2)-928\ \text{cm.}^{-1} \quad (1)$$
$$CO_2^*(\nu_3)+H_2O$$
$$\rightleftharpoons CO_2+H_2O^*(\nu_2)+754\ \text{cm.}^{-1} \quad (2)$$
$$CO_2^*(\nu_3)+H_2O$$
$$\rightleftharpoons CO_2^*(\nu_2)+H_2O^*(\nu_2)+87\ \text{cm.}^{-1} \quad (3)$$
$$N_2^*+H_2O$$
$$\rightleftharpoons N_2+H_2O^*(\nu_2)+736\ \text{cm.}^{-1} \quad (4)$$

and so on. What types of relaxation mechanisms should one employ?

As far as research on pure water and the relaxation process is concerned, the questions discussed above are decidedly worth dealing with. In recent years, wave excitation tubes, lasers, supersonics and the results of tests employing other similar methods demonstrate that [9], at room temperature, the vibratory water membrane between $\nu_1$ and $\nu_3$ is tightly coupled (transition probability $P\sim1$ ), and that $P\sim0.11$, between $\nu_1-\nu_3$ and $\nu_2$ , that $P\sim0.47$, between $2\nu_2$ and $\nu_2$ , and that $P\sim0.28-0.47$; between $\nu_2$ and level or normal movement, there are very small changes in the speeds of water relaxation as a function of changes in temperature. The $V$-$T$ probability ($\sim1/3$) at up to 4100K is basically the same as the results for room temperature. As far as the speed of $H_2O(V\text{-}T)\text{-}N_2$ is concerned, at room temperature $P\sim2.3\times10^{-3}$, , when at 2000K, it is $\sim1/350$ . The vibratory dissipation of laser emmision by water is far quicker than other processes. It is possible to recognize that the vibratory energy of water maintains overall equilibrium with normal or level motion.

As far as the basic physical nature of water relaxation reactions is concerned, there have already been done quite a number of investigations. In particular among these, the recent calculations of Shin demonstrate that [10] the strong affinity reaction between water molecules (hydrogen bonds) are capable of forming weakly bonded complexes. In transfers between the vibrations of $H_2O(\nu_2)$ and complexes, the energy difference is absorbed in rotational movement of the water molecules. In this mechanism, the calculated low 13 temperature (200-400K) relaxation speed agrees very well with experiments. Moreover, at high temperatures, the $V\text{-}R$ energy transfer mechanism is the main one. This type of calculation for 2000-4000K relaxation speeds is in line with data for wave excitation tubes. Due to the fact that the common functions of these two types of mechanisms are present, in the vicinity of 600K, $P$ has an extreme small value that is approximately 0.1.

Due to the fact that the vibratory relaxation speeds for water are extremely fast, over all, one can take the vibrations of water and see them as normal or level motion equilibrium. In this way, $CO_2^*(\nu_2)$ and $N_2^*$ have the energy of transition $V\text{-}V$ to $H_2O^*(\nu_2)$, and are then completely equivalent to $CO_2(\nu_2 \to T)\text{-}H_2O$ and $N_2(v \to T)\text{-}H_2O$. It is only in the cases of the speeds between $K(\nu_2 \to T)\text{-}H_2O$ and $K\nu_2 \to \nu_H$ and between $K(\nu_N \to T)\text{-}H_2O$ and $K\nu_N \to \nu_H$ that there are conversion factors

$$\frac{1-e^{-\theta_2/T}}{1-e^{-\theta_H/T}} \quad \text{and} \quad \frac{1-e^{-\theta_N/T}}{1-e^{-\theta_H/T}}.$$

At 300, 1000, and 2000K, they are respectively 0.960, 1.0005; 0.686, 1.073; and, 0.559, 1.191. With the mechanism $V\text{-}V$ one obtains the data used in the relaxation process for the $V\text{-}V$ mechanism, and, with the $V\text{-}T$ mechanism, one obtains the data used in the $V\text{-}T$ relaxation process. The results are exactly the same. Moreover, $CO_2(\nu_3 \to 3\nu_2)\text{-}H_2O$ and $\nu_3 \to \nu_2 + \nu_H$, speaking in terms of their basic natures, are different. During these processes, they supply different energies of level or ordinary motion (in a later process, $\nu_H$ obtains an energy which is also similar to that provided in level or ordinary motion). Considering the equilibrium of $\nu_H$ and ordinary motion, the conversion factor for the speeds of the two mechanisms is

$$\frac{1-e^{-\theta_H/T}}{(1-e^{-\theta_2/T})^2},$$

For 300, 450, 600, 1000, and 1500 K, these are respectively 1.086, 1.279, 1.536, 2.361, and 3.506. Because of this, Henderson and others [I:83] made use of data obtained for 450 K from the last of the mechanisms, and this made it possible to make use of the results from the former of the mechanisms [I:26] to make mutual comparisons. However, in spite of the fact that, at relatively low temperatures, the data collected for the two mechanisms are not greatly different, depending on which type of relaxation process mechanism the data used comes from, the results certainly are different. It is worth rejoicing about the fact that, in $CO_2$ laser systems, no very clear or precise consideration has been given to $CO_2(\nu_3 \rightarrow \nu_1, \nu_2)-H_2O$. However, it certainly will not have any great effect. Because of this fact, we simply take water and look at it as a collision accompaniment.

## III. ON THE RESONANT TRANSFER ENERGY BETWEEN $\nu_1$ AND $\nu_2$ FOR $CO_2$

This process involves the laser output dissipation for lower energy levels of $CO_2$ lasers and its importance goes without saying. Before the invention of lasers, there was no way, as far as these processes were concerned, to carry out experimental research. Recently, people have carried out a number of theoretical and experimental studies; however, they are still very inadequate. These experiments can be divided into three types. One is making precise measurements of the capabilities of laser instruments using theoretical models to indirectly estimate the speed of $\nu_1 \rightarrow 2\nu_2$ [I:95-97]. The results of this are derived from the theoretical model. In the analysis, whether or not the other speed data used are sensitive to changes in relaxation speeds by measured parameters, is very hard to determine precisely from the results. The results from different people are capable of differing two orders of magnitude. The second problem is the gain measurements for pulse discharge lasers [I:44, 90-92]. In experiments, there is no way to precisely determine the final states of reactions. It is only possible to obtain an average result. In the same way, it is necessary to have an appropriate experimental model in order to analyze them. Moreover, one needs the influences on the other speed processes (such as a number of processes relating to speed chiasma relaxation, rotational relaxation , pulse discharge, and electron collisions) in order to do a detailed analysis. Different peoples' analyses are often very different. The third problem is the laser double resonance law [I:88,93]. It is capable of precisely measuring the particle count and this measured data can be directly related to the relaxation process. However, it is also only capable of directly reaching speeds of $10^00 \rightarrow 02^00$ . It is also necessary, as concerns a number of high speed processes which are capable of directly giving rise to changes in the involved energy level particle counts, such as rotational relaxation and Raman reactions, to make appropriate analyses. The principal theoretical works are Sharma [I:89], (SB theory) and Seeber [I:98] (improved SSH theory). From theoretical calculations it is possible to arrive at speeds for each possible type of reaction. It is experiments for which there is no way to make measurements. Because of the relative values of the speeds for different reactions as obtained from theory, what is needed is experimental analysis. As far as two types of theoretical results are concerned, besides the individual separate reactions, their relative differences are very large. Different experimenters often make use of different theoretical results in order to explain and support their own results.

In actuality, the laser output dissipation of $CO_2(10^00)$ has a very complicated mechanism

$$CO_2(10^00)+M \rightleftharpoons CO_2(02^00)+M+102.8\ cm.^{-1} \qquad (8)$$

$$CO_2(10^00)+M \rightleftharpoons CO_2(02^20)+M+52.7\ cm.^{-1} \qquad (9)$$ 14

$$CO_2(02^20)+M \rightleftharpoons CO_2(02^00)+M+50.1\ cm.^{-1} \qquad (10)$$

$$CO_2(10^00)+CO_2(00^00) \rightleftharpoons CO_2(01^10)+CO_2(01^10)+53.7\ cm.^{-1}$$

$$CO_2(02^00)+CO_2(00^00) \rightleftharpoons CO_2(01^10)+CO_2(01^10)-49.1\ cm.^{-1}$$

$$CO_2(02^20)+CO_2(00^00) \rightleftharpoons CO_2(01^10)+CO_2(01^10)+1.0\ cm.^{-1}$$

(1) 表3 $CO_2$ 激光体系中各种过程的速率(室温,除 $\tau_\nu^{-1}$ 为 秒$^{-1}$ 外,均为 托$^{-1}$·秒$^{-1}$)

| $X_C:X_N:X_H=0.08:0.91:0.01$ | | | $\nu_1\rightarrow 2\nu_2$ | (2) 振型内 V-V | $H\rightarrow T$ | $\tau_\nu^{-1}$ (3) ($I=10^3$ 瓦/厘米$^2$) |
|---|---|---|---|---|---|---|
| $\nu_3\rightarrow T$ | $\nu_3\rightarrow\nu_1,\ \nu_2$ | $\nu_3\rightarrow\nu_N$ | | | | |
| $4.2\times10^3$ | $3.7\times10^3$ | $1.3\times10^4$ | $(1-5)\times10^5$ | $10^5-10^6$ | $\sim1\times10^7$ | $\sim8\times10^4$ |

1. Table 3 Speeds of Various Types of Processes in $CO_2$ Laser Systems (Room temperature, except for $\tau_\nu^{-1}$ being seconds $^{-1}$ , in all cases, is drag or shaft E $^{-1}$ . seconds $^{-1}$ ) 2. Interior Vibration Form 3. Watts/sq. cm

Moreover, what primarily concerns us is the speed of the evacuated laser lower energy level $10^00$ , that is, the speed of $10^00\rightarrow 2(01^10)$.

In the laser dynamics research about which we are interested, it has been suggested that we adopt for use the approximation of an equilibrium between $\nu_1$ and $\nu_2$ . The basis for this is that experimental measurements have arrived at the fact that (5), with a speed of 300K, is $4\times10^5$ drag $^{-1}$. seconds $^{-1}$ . On the basis of theoretical calculations [1:89,93,98], the speed of (9) is $1.1\times10^5$ . (8) and (9) are approximately equivalent. Also, in some situations, one also has (6)+(10) and other such relaxation processes which cause the laser output dissipation of $10^00$ to increase in speed. At times when there are radiation fields involved, the particle count created in the process of stimulating radiation can be extracted for operational purposes, and it is possible to use the equivalent speed $\tau_\nu^{-1}$ in order to make estimated calculations [11]. In a natural light chamber in which the strength of the illumination was 380 watts/sq.cm, $\tau_\nu^{-1}$ was calculated out to be approximately $7.1\times10^4$ seconds $^{-1}$ [12] (see Table 3). It appears as though, except for times when the intensity of the light is exceptionally strong (> $10^4$ watts/sq.cm), it is always possible to adopt the approximation of an equilibrium between $\nu_1$ and $\nu_2$ .

## IV. SIMILARITIES AND DIFFERENCES IN THE SPEEDS OF RELAXATION IN COMPRESSION FLOWS AND EXPANSION FLOWS

In 1964, Hurle and others [13] discovered that reflected shock waves of heated $N_2$ in jet tube expansion flows require one to take the relaxation duration measured in excitation or shock wave compression flows and greatly shorten it ( $\phi$ times). Only then is it possible to explain the phenomena in expansion wave experiments. Moreover, excitation or shock wave compression flows and the data obtained from other experimental methods (supersonic, photoemissive and so on) are in line with each other. This startling result immediately caught peoples' attention and promoted experimental and theoretical research. Concerning this matter, Hurle carried out a detailed evaluation [16]. At the high temperatures which are made use of in compression flows, the high vibratory kinetic energy levels for non-harmonic strengths will show obvious concentrations. Moreover, as far as the energy relaxation processes which are obtained when one deals with the relaxation speeds gotten from expansion flows are concerned, when one takes the resonating particles and assumes them to be the basis, it is recognized that the interior of the vibratory form or mode is in a quasi-balanced distribution ( $V$-$V$ speeds are far greater than $V$-$T$ speeds) [17]. Through mutual comparisons with compression flow experiments, Treanor and others developed the theoretical analysis of non-resonant particle systems [18]. Due to the fact that $V$-$V$ is very much faster than the $V$-$T$ process, the vibratory distribution function will show distortions, causing the vibratory temperatures which are equivalent to the 0->1 transition to go down. Therefore, it will seem as if the speed of the excitation output dissipation has been speeded up.

The two types of systems on which relatively broad research has been done are CO and $N_2$. A detailed analysis of the results of experiments with CO demonstratesthat the unusually large $\phi$ values which were obtained by Russo and his coworkers are due to their possible introduction of small amounts of materials into samples. In wave excitation tube experiments, it was extremely easy to introduce CO. This was particularly true under high temperatures for H atoms produced by ionization, and, on the relaxation of CO, this produced very great effects. The experiments of Von Rosenberg and others demonstrate [14] that, in systems which include 5% CO, the introduction of 100 ppm of $H_2$ will then cause $\phi$ to go to 10, and 500 ppm will cause it to go to 100. The recent experiments of Nasser and others have been relatively detailed [15], and they have given their attention to the various kinds of related factors which influence the experiments. They have arrived at $\phi\sim2$. Moreover, they definitely gave their attention to a comparison with non-resonsant particle theory and gave consideration to the influences of experimental precision and the speed of $V$-$V$ on theoretical calculations. They recognize that theory and experimentation match well with each other.

Impurities are not capable of having that large an effect on $N_2$ expansion flows. In non-resonant reactions under $N_2$ expansion flow conditions, it is not possible to create $\phi > 5$. The fact that a number of people have obtained large $\phi$ values is due to the error from the sodium line inversion method of measuring vibration temperatures. Originally, everyone recognized that $Na(^2S)+N_2(v-7.8)\rightarrow Na(^2P)+N_2(v-0)$ is resonant; that is, that the sodium electron temperature $T_e$ and the $T_v$ resonance temperature are equivalent. In 1972, MacDonald [19], making use of the non-resonant energy transfer model between $Na$-$N_2$ which was presented in [20], discovered that, when $T_v>T$, $T_v$ was obviously larger than $T_e$. He used this model to explain anew the experiments of Hurle and his coworkers as well as his own experiments. In all cases, he arrived at the result $\phi_{N_2}\sim1$. Kewley [21] took this result and used it with the experiments which Hurle had begun [13]. He also arrived at $\phi_{N_2}\sim1.4$. This can be explained by a non-resonant reaction. (15)

Expansion flow experiments on $CO_2$ systems are very few [2]. The results of experiments which make use of non-resonant models to handle in a new way the sodium line inversion method make it possible to obtain the result $\phi\sim1$.

Summing up what we have talked about above, in expansion flows, it is entirely possible to make use of pressure compression experiments to obtain measurements for relaxation speeds, except for the errors introduced by data handling and extraneous materials. Between the two of these factors, it is possible to have errors and differences in relaxation speeds with these coming mainly from non-resonance. Also, for the temperatures in which we are interested

(<2000K), non-resonant effects are not large [17]. In reality, non-equilibrium expansion flow calculations and experiments agree very well [I:2]. To explain it in another way, numerical data on relaxation in expansion flows is also usable.

## V. ON "LOCALIZED EQUILIBRIUM" INSIDE VIBRATION FORMS

Given the assumption of resonant particles, the vibratory form $V\text{-}V$ transfer is precisely resonant, and its transition probability $\sim 1$ . However, because of the non-resonant reaction, for the interval between adjacent vibratory kinetic energy levels $\Delta E_v \sim 2\omega_e x_e (v-1)$ , $v$ is the upper energy level quantum number, and $\omega_e x_e$ is the spectrum constant. A number of molecules, particularly those molecules that contain hydrogen, have a $\omega_e x_e$ which is quite large. They have a high vibration shock wave form, and their non-resonance is completely obvious. This is precisely the problem of whether or not the overall energy can maintain localized equilibrium within a vibratory form or mode. The key to this is whether or not, when comparisons are made between the $V\text{-}V$ exchange within a vibrational form and other processes within the system, the former is much faster than the latter. Theoretical analyses of CO and chemical lasers indicates that, within vibration modes, the $V\text{-}V$ energy transfer speed has a considerable influence on its nature. In the case of $CO_2$ pulse excitation lasers, there are people who also acknowledge that it is possible to destroy the local equilibrium within vibration forms [I·95].

In recent years, in conjunction with laser research, theoretical and experimental research has been carried out concerning the $V\text{-}V$ energy transfer within vibration forms for a series of molecules. They arrived at $AB(v)+AB(0) \rightleftharpoons AB(v-1)+AB(1)$ speeds for different $v$ and under different temperature conditions. If HF[22], at room temperature, has $v$ = 2,3,4 respectively; it is 0.68, 1.4, and 1.2x $10^6$ (drag or shaft G $^{-1}$. seconds $^{-1}$ . Same as below). The HCl[23] $v$ = 2 reverse reaction speed, at room temperature, is 1.4 x $10^{6}$ , and, at 700K, is 3.2x $10^4$; . HBr[24] $v$ = 2, at room temperature, is 1.7x $10^5$, and ., at 600K, is 5x $10^4$ . DF[25], at room temperature, has a reverse reaction speed which, for v=2, is 7x$10^5$, and, for v>2, is 1.61$^{2\to}\times 7\times 10^5$.

For CO[26], at 100K, $v$ = 2's 6.2x $10^5 \rightarrow v$ = 7's 2.5x $10^9$ . At 300K, $v$ =2's 6.2x $10^4 \rightarrow v$ = 11's 1.5x $10^3$ . At 500K, $v$ = 2's 2.8x $10^4 \rightarrow v$ = 12's 1.4x $10^5$ . It is possible to see that, as far as low vibration energy levels are concerned, $V$-$V$ speeds within vibration forms reach $10^5 \sim 10^6$. Compared to the generality of $V$-$V$ and $V$-$T$ speeds, this is very much faster. Moreover, when $v$ is large, the speed is only of the $10^3$ order of magnitude. This is certainly obviously faster than the other processes.

$CO_2$ molecules have three vibration forms or modes (one of them is a two degree arrangement of simple forms). Between different vibration forms, there exist complicated energy transfer processes. Up to the present time, we have not seen direct measurements of $V$-$V$ speed within vibration modes. Burak, et al., measured the speed of $00^01+01^10\rightarrow01^11$ at room temperature, to be 5.3x $10^6$ [27]. It occurs between the different vibration forms within molecules. However, this result "wipes off" the upper energy levels of lasers. As *concerns this*

process, Doyennett and others measured the temperature relationship to be room temperature 3.7x $10^6$ ->900K 1.3x $10^6$ [28]. What is required is direct measurements of $V$-$V$ speeds within the vibration forms of $CO_2$ due to the fact that the non-resonant characteristics of the various vibration forms of $CO_2$ are all small (corresponding to the $\nu_1$、$\nu_2$、$\nu_3$ of $\omega_e x_e$ , respectively 0.3, 1.3, and 12.5 cm$^{-1}$ . As a comparison, CO HCl,HF. and HBr are respectively 15.16, 52.05, 45.71, and 45.21 , and because, as far as the reciprical applications of $CO_2$ are concerned, the moments of inertia are all ordinary, consequently, it is predicted that the $V$-$V$ speed within the vibration forms will be $10^5 \sim 10^6$ Under the general run of conditions (vibration, temperature, and probability), the only clear concentrations there are are the several relatively small vibrational non-resonant energy levels on the bottom surface. Because of this, when radiation fields are not too strong (< $10^4$ watts/sq.cm), and when the pulse width is larger than milliseconds (see Table 3), it is recognized that there exist within the vibration forms localized equilibria, and that this will be a good approximation. At this time, one should make use of energy relaxation processes. Moreover, at times when the vibrational forms are severely out of equilibrium, that is, the $V$-$V$ speeds within the vibration forms are much smaller than for other processes, it is possible to recognize that the vibration is only "frozen" at the lowest level of vibrational energy. At this time, one should make use of the particle count process [17].

## VI. ON EQUILIBRIUM BETWEEN ROTATIONAL ENERGY LEVELS

All molecular light excitation occurs between certain specific rotational energy levels. Obviously, rotational relaxation has an influence on the capabilities of lasers. As far as transitional competition in lasers is concerned, the reactions involved in the burning of holes all have their physical basis in rotational 16
relaxation. In recent years, in-depth research has been carried out appropriate to a need in the area of the clusterings of laser nuclei and the influences which rotational relaxation and short pulse lasers have on this [29]. The research makes clear that milli-microsecond pulse lasers and all the excitation energies and pulse wave forms which they are capable of picking up and putting out are very greatly influenced by the rotational relaxation interval $\tau_R$. Under classical conditions, it is only when the pulse width is larger than 15 $\tau_R$ that one is able to approximately assert that the degree of rotational freedom lies at equilibrium. When doing research on the rotational energy of HF, it was also discovered that high $V$-$R$ rotational energy excitation states are not able to reach rotational equilibrium [30].

There are people who have discovered that the vibrational relaxation periods of the 20 rotational energy levels for $J$ = 4 to 46 in $CO_2(10^00)$ vary with changes in $J$, and they recognize that the rotation which exists is not in equilibrium. However, the results of these experiments are still under discussion [31].

As far as whether or not one sees equilibrium between rotational energy levels is concerned, basically speaking, it depends on the rotational relaxation speed relative to the size of other processes. For a long time, a large amount of theoretical calculations and experimental measurements have been done on rotational relaxation [I:13]. It is already known that the rotational relaxations for double atom or multiple atom molecules are all very fast, developing rotational transition collision numbers of $Z_R$ <10. It is only for molecules containing hydrogen that it is possible to reach the $Z_R$ fist and second orders of magnitude. As concerns $CO_2$, , if one takes as the collision accompaniments and the rotational $CO_2$, $N_2$, He relaxation speeds for their $00^01$ energy levels to be respectively 1.3, 1.2, and 0.6x $10^7$ drag or shaft $G^{-1}$ . seconds $^{-1}$ [32], then, they are of the same order of magnitude as the gas collision frequencies, and, in addition, one discovers that the speeds vary with changes in $J$ . In the vicinity of $J$ = 19, there is an extremely large value. As concerns the relationship of temperature, we have not seen experimental results for $CO_2$ . However, research concerning other systems makes it clear that the speed of rotational relaxation does not follow changes in temperature to any great degree. It is worth noting that Rabitz and others have made theoretical analyses of rotational relaxation speeds under supersonic conditions and for free jets, and wave excitation tubes. This analysis demonstrates that the speeds obtained through the three methods are the same at low temperatures. However, at relatively high temperatures (>200K), they differ from each other [33].

In extremely short pulse (pulse widths smaller than 15 $\tau_R$ ) laser apparatuses, it is possible to take all the vibration relaxation processes and view them as frozen, only considering the influence of rotational relaxation. Besides this, as far as $CO_2$ systems are concerned, it is only when radiation fields are extremely strong (>$10^5$~$10^6$ watts/sq.cm) that it is possible to see the occurrence of rotational non-equilibrium reactions (see Table 3). Generally, it is possible in all cases to adopt the assumption of rotational equilibrium. In the case of molecules that contain hydrogen, the range in which it is appropriate to make this assumption needs to be contracted.

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