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LASER ATMOSPHERIC PROPAGATION ON KINETICS

C. A. Brau

Avco Everett Research Laboratory, Incorporated

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LASER ATMOSPHERIC PROPAGATION KINETICS

SEMI-ANNUAL TECHNICAL REPORT

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FOREWORD

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ABSTRACT

An analytical model has been developed describing the atmospheric absorption of DF laser energy and the subsequent kinetic processes of energy exchange. For eight representative strong laser transitions, the atmospheric absorbers with energy levels and absorption cross sections have been specified. The analytical kinetic model describing the kinetics of absorption by N_2O , CO_2 , CH_4 and HDO - H_2O has been developed and rate constants have been selected for use in the calculation.

Preliminary results of the quantitative determination of the atmospheric temperature change resulting from absorption by N_2O are presented. An assessment of the sea level kinetic effects of N_2O in heating the atmosphere is given using a simple square wave pulse shape. Two limiting concentrations of water have been used and the laser energy has been varied over several orders of magnitude.

TABLE OF CONTENTS

S	e	с	t	i	0	n	
_	-	-		_	-	-	

Pa	ge
	—

	roreword	ii	
	Abstract		
	List of Illustrations		
Ι	INTRODUCTION		
II	SPECTROSCOPY		
	 A. Selection of Laser Transitions B. Selection of Atmospheric Absorbers and Absorption Coefficients 	3	
III	KINETICS	- 5	
	 A. Kinetics of Absorption by N₂ B. Kinetics of Absorption by CO₂ C. Kinetics of Absorption by H₂O D. Kinetics of Absorption by N₂O E. Kinetics of Absorption by CH₄ F. Kinetics of Absorption by HDO 	5 5 7 9 14	
IV	RESULTS	10	
	REFERENCES	25	

-iv-

LIST OF ILLUSTRATIONS

Figure		Page
1	Kinetics of N ₂ Continuum Absorption	6
2	Kinetics of $CO_2(v_3)$ Absorption	8
3	Kinetics of $H_2O(v_2)$ Absorption	10
4	Kinetics of N ₂ O Absorption	12
5	Kinetics of CH ₄ Absorption	15
6	Kinetics of HDO Absorption	18
7	Translational Temperature Rise Due to N ₂ O Absorption of 7 DF Laser Lines	20
8	Effect of Water Concentration on Temperature Rise for P ₃ (8) DF Line With N ₂ O Absorption	21
9	Distribution of Power for Absorption by N_2O of the P3(8) DF Laser Line as Function of Incident Power. $[H_2O]= 20$ Torr.	22
10	Distribution of Power for Absorption by N_2O of the P ₃ (8) DF Laser Line as a Function of Incident Power. $[H_2O]$ = 2 Torr	23

۷

I. INTRODUCTION

The purpose of this program is to develop an analytical model describing the atmospheric absorption of laser energy and the subsequent kinetic processes of energy exchange. The final results of this effort are to be the quantitative determination of the atmospheric temperature change resulting from this absorption.

The major effort to date has been concentrated on the DF laser system. Eight representative strong laser transitions have been selected. The atmospheric absorbers, energy levels and absorption cross sections have been specified. The analytical kinetic model has been developed and rate constants have been selected for use in the calculation. With a simple square wave pulse shape and 30 μ sec pulse length, the model has been used to give a preliminary assessment of the sea level kinetic effects of N₂O in heating the atmosphere. Two limiting concentrations of water have been used and the laser energy has been varied over several orders of magnitude. The results are shown and discussed below.

II. SPECTROSCOPY

A. SELECTION OF LASER TRANSITIONS

The eight DF laser transitions shown below in Table I were chosen from the experimental work of Deutsch⁽¹⁾ and Basov et al.⁽²⁾ Reference 1 which contains the most accurate experimental measurements of line position (\pm .08 cm⁻¹) was used to determine the transition frequency, and the relative energy data of Ref. 2 were used to select lines of strong output. Care was employed to ensure that all known atmospheric absorbers were covered by these lines.

TABLE I

DF LASER TRANSITIONS

Laser Line Identification	Laser Frequency (cm ⁻¹)	Relative Energy*
2P(8)	2631.09	2, 37
2P(9)	2605.87	2.68
2P(10)	2580. 16	4.24
2P(11)	2553.97	3.46
3P(8)	2546.37	2. 74
3P (9)	2521.81	5. 38
3P (10)	2496.61	3, 35
2P(11)	2471.34	2.26

*Energy of 1P (10) transition is taken as 1.

B. SELECTION OF ATMCS PHERIC ABSORBERS AND ABSORPTION COEFFICIENTS

The atmospheric absorbers of importance at DF laser wavelengths are N₂O, CH₄, H₂O, HDO, and CO₂. This is confirmed by both absorption cell experiments⁽³⁾ and theoretical calculations (based on experimental data).⁽⁴⁾ Reference 4 is an AFCRL compilation of the molecular spectroscopic parameters for a number of infrared-active molecules (including those listed above) which occur naturally in the terrestrial atmosphere. Parameters included in the compilation for each absorption line are: frequency, intensity, half-width, energy of the lower state of the transition, vibration and rotational identifications of the upper and lower energy states, an isotopic identification, and a molecule identification. We have written a code which sorts the AFCRL data according to absorbing molecules over a given frequency interval and calculates the absorption cross section for the absorbing molecule at the laser frequency of interest.

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 N_2O cross sections computed by this program are in excellent agreement with the absorption cell measurements of Ref. 3 for all the laser transitions considered. All results shown below are for N2O. For CH_4 , the agreement is not as good, averaging about a factor of 3-4. For CO2, where the absorption is due to CO₂ lines of the 4. 3μ band hundreds of wave numbers removed from the laser frequency, we will use the experimental results which fall in between the calculated results using a Lorentz line shape (too high) and the best experimental line shape fit to CO_2 absorption data (too low)(5) The theoretical calculations and experimental results are in complete disagreement for HDO-H₂O. Because the experimental absorption cross sections for HDO were obtained by subtracting the very large absorption due to D_2O from the measured total absorption, we assume the error to be here and have chosen to use the calculated values which for H₂O are in agreement with data of Benedict. (6) These uncertainties in the cross sections for CH4, CO2, and HDO-H2O are not discussed here in detail because no results for these molecules are presented in this report.

The major absorber at DF wavelengths is N_2O and the preliminary results presented below are for N_2O . Results including all absorbers will be presented in a later report. It should be noted that these calculations of absorption cross section are only very weakly dependent on the experimental uncertainty (0.08 cm⁻¹) in the determination of the exact position of the laser transition. Because we have shown the cross section to be essentially unaffected by shifting the laser frequency by ± 0.08 cm⁻¹, all results are shown assuming the laser frequency exactly as given in Table II.

TABLE II

ABSORPTION CROSS SECTIONS FOR N₂O AT DF LASER FREQUENCIES

$N_2O(cm^2)$

2P (8)	0
2P(9)	3.6×10^{-22}
2P(10)	2.9×10^{-20}
2P(11)	1.0×10^{-20}
3P (8)	2.9×10^{-20}
3P (9)	4.7×10^{-22}
3P (10)	$\frac{1}{2}$ 4 x 10 - 22
3P(11)	$4.2 - 10^{-21}$
\/	4. Z X 10-21

-4-

III. KINETICS

A. KINETICS OF ABSORPTION BY N2

DF laser radiation is absorbed by N_2 on the collision induced vibrational continuum band centered around 4.3 μ m:

$$N_2(v=0) + h\nu + M \rightarrow N_2(v=1) + M + \Delta E$$
. (1)

The excess energy $\Delta E = h\nu - E_{vib} \sim 250 \text{ cm}^{-1}$ appears immediately as translational and rotational heating of the N₂ and M molecules

The relaxation of $N_2(v=1)$ by the dominant atmospheric species (N_2, O_2, H_2O) has been extensively studied as a result of interest in the CO_2-N_2 laser. V-T deactivation of $N_2(v=1)$ by N_2 and O_2 and V-V transfer to O_2 is extremely slow. The most important relaxation path is provided by H_2O . It has not been established directly whether the quenching of N_2 by H_2O proceeds by a V-T (or vibration to rotation) process, or by V-V transfer to the v_2 mode of H_2O ,

$$N_2(v=1) + H_2O(000) \rightarrow N_2(v=0) + H_2O(010) + 735 \text{ cm}^{-1}$$
 (2)

However, the subsequent relaxation of H_2O (010) is so fast that for practical purposes it does not matter.

These processes are summarized in Fig. 1. The time scales for the various processes in this and the following sections are predicted on an atmosphere composed of

 $N_2 (2 \times 10^{19} \text{ molecules/cm}^3), O_2 (5 \times 10^{18} \text{ molecules/cm}^3), H_2O (3 \times 10^{17} \text{ molecules/cm}^3),$

at a temperature of 300° K. The amount of energy which appears as thermal (translational + rotational) energy at each step is also indicated. We see that under the above conditions, absorption on the N₂ continuum band results in a small amount of essentially instantaneous heating followed by slow heating on the N₂ relaxation time scale, which is of the order of 8 x 10⁻⁴ s.

B. KINETICS OF ABSORPTION BY CO2

DF laser radiation is absorbed by CO₂ on the ν_3 fundamental band centered at 4. $3\mu m$:

$$CO_2 (000) + h\nu \rightarrow CO_2 (001) + \Delta E$$
. (3)



Fig. 1 Kinetics of N₂ Continuum Absorption

-6-

The absorption takes place principally in the far wings of the lines corresponding to low thermally populated, rotational levels. Thus most of the excess energy ΔE (~250 cm⁻¹) appears instantaneously as translational energy of the CO₂ and collisional broadening molecules.

The relaxation of $CO_2(001)$ by the dominant atmospheric species (N_2, O_2, H_2O) has been extensively studied as a result of interest in the CO_2-N_2 laser. Relaxation takes place principally via intermolecular V-V transfer to N_2 ,

$$CO_2 (001) + N_2 (v=0) \rightarrow CO_2 (000) + N_2 (v=1) - 18 \text{ cm}^{-1}$$
 (4)

The subsequent relaxation of $N_2(v=1)$ is described above.

These processes are summarized in Fig. 2, where the relaxation times correspond to the same atmospheric conditions as in Fig. 1. Aside from the small amount of heat released by the absorption process, the overwhelming effect of absorption by CO_2 is to heat the gas on a slow time scale (~10⁻³s) corresponding to the relaxation of the N₂(v=1) level.

C. KINETICS OF ABSORPTION BY H₂O

The absorption of DF radiation by H_2O , while somewhat controversial, as mentioned above, is alleged to occur on the v_2 fundamental transition

$$H_2O(000) + h\nu \rightarrow H_2O(010) + \Delta E$$
. (5)

The relatively large excess energy ($\Delta E \sim 900 \text{ cm}^{-1}$) appears as translational and rotational energy of the H₂O molecule, and is presumed to be thermalized instantaneously.

The relaxation of the $H_2O(\nu_2)$ mode has been studied experimentally for a long time, and while considerable uncertainty remains for some of the important rates, a broad understanding is possible. The most important processes for the relaxation of $H_2O(\nu_2)$ are near resonant V-V transfer to O_2 ,

$$H_2O(010) + O_2(v=0) \rightarrow H_2O(000) + O_2(v=1) + 38 \text{ cm}^{-1}$$
. (6)

and T-V quenching,

$$H_2O(010) + M \rightarrow H_2O(000) + M + 1595 \text{ cm}^{-1}$$
, (7)

where $M = N_2$, O_2 , and (most importantly) H_2O itself. There is considerable scatter in the data on the T-V quenching of $H_2O(\nu_2)$ by H_2O , but the rate is apparently quite fast, of the order of $2 \times 10-12-5 \times 10-11 \text{ cm}^3/\text{s}$, (about 10-100 collisions). The most recent data favor the fastest rate. The data on V-V transfer to O₂ (reaction (6)) are somewhat confused due to apparent errors in most of the papers. The correct rate seems to be about 1.5 $\times 10^{-12} \text{ cm}^3/\text{s}$.

-7-



Fig. 2 Kinetics of $C\bar{U}_2(\nu_3)$ Absorption

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the majority) favor the slowest rate. The energy which is transferred to O_2 relaxes relatively slowly by T-V quenching of O_2 by H₂O,

$$O_2(v=1) + H_2O(000) \rightarrow O_2(v=0) + H_2O(000) + 1556 \text{ cm}^{-1}$$
, (8)

and by transfer back to H_2O followed by quenching of the H_2O .

These processes are summarized in Fig. 3, where the times indicated correspond to the atmospheric conditions of Figs. 1 and 2. The absorption of a laser photon leads to some immediate heating (on a time of the order of the rotational relaxation time) as indicated. T-V quenching of the H₂O leads to further very rapid heating (on a time scale of the order of 10⁻⁷ to 10⁻⁶s. The energy which is transferred to O₂ produces heating on a somewhat larger time scale, of the order of 10⁻⁵s. The extent of heating occurring on the fast and slow time scales depends on the relative rates of T-V quenching and V-V transfer to O₂. If the faster H₂O/O₂ V-V transfer rate and/or slower H₂O/H₂O T-V quenching rate is correct, or if the humidity is low (as it will surely be at higher altitudes) then the bulk of the H₂O vibrational energy will be transferred to O₂. This will shift the heating to significantly lo. Ger times. These uncertainties become even more important for the absorption of CO laser radiation, since H₂O(ν_2) is

D. KINETICS OF ABSORPTION BY N20

DF laser radiation is absorbed by $\rm N_2O$ principally on the ν_2 overtone transition,

$$N_2 O(000) + h\nu \rightarrow N_2 O(200) + \Delta E$$
, (9)

and the combination band transition

$$N_2 O(000) + h\nu \rightarrow N_2 O(12^{\ell}0) + \Delta E.$$
 (10)

A small amount of absorption takes place on the corresponding transitions from the N_2O (01'0) level, but this may be ignored.

Most of the available data on N₂O vibrational relaxation were obtained in pure N₂O and N₂O/N₂ mixtures, and do not shed much light on what are felt to be the most important processes in the atmosphere. To identify the most important processes we note that N₂O is very similar to CO₂. Both are linear triatomic molecules with comparable masses. It is important to note, however, that mode v_1 is IR active that is, it possesses a dipole moment - in N₂O, whereas it is not IR active in CO₂. This is because CO₂ is a symmetric molecule whereas N₂O is not, having the configuration N-N-O. It is also important to remember that the levels 10°0 and 02°0 are strongly coupled by Fermi resonance in CO₂ but not in N₂O. Available data indicate that modes v_1 and v_2 of CO₂ are rapidly coupled by collisions and may be assumed to relax together, but that mode v_3 is only weakly coupled to the other two and



Fig. 3 Kinetics of $H_2O(v_2)$ Absorption

relaxes by itself. All the data concern mixtures rich in CO_2 , so that modes v_1 and v_2 may be coupled by intermolecular V-V transfer processes of the type

$$CO_{2} (10^{\circ}0) + CO_{2} (00^{\circ}0) \rightarrow 2 CO_{2} (01^{\circ}0)$$

or $\rightarrow CO_{2} (00^{\circ}0) + CO_{2} (02^{\ell}0)$. (11)

It is also suggested that in dilute mixtures coupling via intramolecular processes,

$$CO_2 (10^{\circ}0) + M \rightarrow CO_2 (02^{\ell}0) + M$$
 (12)

where $M \pm CO_2$, is rapid due to the Fermi resonance which mixes the levels (10⁰0) and (02⁰0).

There is no corresponding evidence of rapid coupling of modes v_1 and v_2 in N₂O in the atmosphere. Intermolecular V-V processes similar to (11) are unimportant due to the high dilution, and modes v_1 and v_2 are not mixed by Fermi resonance. The acoustical data have been interpreted in terms of the simultaneous relaxation of modes v_1 and v_2 , but the data are not compelling. For lack of evidence we shall make the same approximation.

The evidence does show, however, that mode v_3 is only weakly coupled to modes v_1 and v_2 . Results obtained in $N_2 \tilde{O}/N_2$ mixtures indicate that quenching of mode v_3 by N₂ requires about 10⁵ collisions which is only about a factor of two factor than the corresponding process in CO₂. It is not known to which level the CO₂ (00^o1) level is guenched, although the data of Cannemijer indicate that it is the CO₂ $(03\ell 0)$ level in CO₂-CO₂ collisions and the CO₂ $(02\ell 0)$ level in CO₂-rare gas collisions. However, even if it is the near-resonant 04 0 or other nearby levels in N_2O , detailed balance indicates that the reverse rate, coupling modes v_1 and v_2 to mode v_3 in collisions with N₂, will be slow. This is supported by the experiments of Yardley, who excites N_2O mode v_3 in mixtures with N2. He observes that N2O mode v_3 rapidly couples to N2 by V-V transfer in about 1100 collisions. However, at the end of this (short) time the extent of residual excitation in mode v_3 indicates that modes v_1 and v_2 have not been excited by either direct intramolecular V-V processes or intermolecular V-V transfer back from N₂. Quenching of CO_2^* (ν_3) to modes ν_1 and ν_2 by H₂O is much faster than by N₂, requiring of the order of 10³ collisions. This is probably because H₂O rotation can absorb much of the nonresonance between CO_2 (00^o1) and CO_2 (mn^l0). However, even this rate of coupling is likely to be much slower than direct quenching of modes v_1 and v_2 by H_2O (see below).

We are therefore led to neglect the coupling of modes v_1 and v_2 to mode v_3 and to assume that modes v_1 and v_2 are rapidly coupled. This leads to the model shown in Fig. 4. According to this model, modes v_1 and v_2 are reduced to four lumped levels, each consisting of several near-resonant levels as indicated by the dotted lines.



Fig. 4 Kinetics of N₂O Absorption

Few of the rates of relaxation of these levels have been measured experimentally. The relaxation of the $N_2O(v_2)$ level has been determined by acoustical and spectrophone techniques and found to be 1.8 x 10^{-14} cm³/s. This is approximately a factor of five faster than the corresponding relaxation rate for $CO_2(v_2)$, as might be expected from the slightly lower vibrational frequency of $N_2O(v_2)$. To scale the rate to different temperatures we assume that the temperature dependence for $N_2O(v_2) + N_2$ is the same as that for $CO_2(v_2) + N_2$. To scale the rate to higher levels we assume the harmonic oscillator rule, which says that for level (0 m⁴ 0) the quenching rate is proportional to m.

Continuing the analogy to CO₂, we would anticipate that the quenching of $N_2O(\nu_2)$ by H₂O should be a very rapid process since the quenching of CO₂(ν_2) requires only about 20 collisions. Two theories have been advanced to explain the rapid quenching of CO₂. Widom and Bauer suggest that CO₂ and H₂O interact chemically, since H₂CO₃ is known to exist in solution. Semiquantitative calculations based on this mechanism give the right order of magnitude for the quenching rate. Sharma suggests that the multipolar interaction between CO₂ and H₂O is responsible. Detailed computations based on this mechanism are also in reasonable agreement with the experimental data. If the latter explanation is correct, a similar mechanism should operate in N₂O-H₂O collisions. On this basis we assume that the rate of quenching of N₂O (01¹0) by H₂O is the same as the measured rate of quenching of CO₂(01¹0) by H₂O at all temperatures. To scale to higher levels, the harmonic oscillator rule is used.

The quenching of $N_2O(v_1)$ is likely to be much slower because of the larger vibrational level spacing, compared with mode v_2 . Provided that modes v_1 and v_2 are closely coupled the direct quenching of mode v_1 can be ignored. However, if they are not so coupled it is necessary to consider what might be the most important processes relaxing mode v_1 . A strong candidate for the dominant role is near-resonant V-V transfer to H_2O :

$$N_2O(10^{\circ}O) + H_2O(000) \rightarrow N_2O(00^{\circ}O) + H_2O(010) - 310 \text{ cm}^{-1}$$
. (13)

Although this reaction might seem far from resonant, H_2O has shown itself capable of a variety of not-so-resonant processes, apparently because a large amount of nonresonance can be made up by the H_2O rotational frequency. Similar reactions to which (13) may be compared include the reactions

$$CS (v=1) + H_2O (000) \rightarrow CS (v=0) + H_2O (010) - 323 \text{ cm}^{-1}$$
, (14)

NO
$$(v=1) + H_2O(000) \rightarrow NO(v=0) + H_2O(010) + 281 \text{ cm}^{-1}$$
, (15)

$$N_2O(00^{\circ}1) + HBr(v=0) \rightarrow N_2O(00^{\circ}0) + HBr(v=1) - 335 cm^{-1}$$
. (16)

These reactions have room temperature rates (in the exothermic direction) equal to $1 \times 10^{-11} \text{ cm}^3/\text{s}$, $2 \times 10^{-12} \text{ cm}^3/\text{s}$, and $2 \times 10^{-12} \text{ cm}^3/\text{s}$ respectively. A rate equal to $10^{-12} \text{ cm}^3/\text{s}$ seems reasonable for reaction (13) in the exothermic direction. This is much slower than the quenching of mode v_2 by H_2O and will be negligible if the modes are coupled. However, if modes v_1 and v_2 are not coupled their rates of relaxation are likely to be quite different.

These processes are summarized in Fig. 4, where the times indicated correspond to the atmospheric conditions of Figs. 1, 2 and 3. Only a small amount of heating accompanies the absorption of a laser photon. The bulk of the heating occurs on a time scale of the order of 2×10^{-7} s, corresponding to the quenching of N₂O(v₂) by H₂O.

E. KINETICS OF ABSORPTION BY CH₄

DF laser radiation is absorbed by CH_4 on the v_4 overtone band

$$CH_{A} (0000) + h\nu \rightarrow CH_{A} (0002) + \Delta E$$
(17)

and the combination band

$$CH_{A}(0000) + h\nu \rightarrow CH_{A}(0101) + \Delta E$$
 (18)

In the experiments which have been done on CH₄ so far, all the vibrational modes have been coupled very rapidly by CH4-CH4 collisions (of the order of 70 collisions to couple modes v_3 and v_4 , and less than 100 collisions to couple modes v_2 and v_4). Since this coupling presumably takes place via intermolecular V-V transfer in high concentrations of CH_4 , the modes are likely to be much more slowly coupled in dilute mixtures of CH₄. On the basis of his experimental data Yardley concludes that the rate of coupling by rare gases is probably at least a factor of ten slower. Nevertheless, we shall assume that all the modes are strongly coupled since there is not enough data on vibrational relaxation in CH4 to justify a more detailed description. Furthermore, the symmetric and asymmetric bending modes, v_2 and v_4 , have comparable vibrational frequencies and are likely to behave similarly, whether coupled or not. The stretching modes, v_1 and v_3 , have much larger vibrational frequencies and probably relax much more slowly than the bending modes. They will therefore have little effect on the relaxation of CH₄ except to increase the effective degeneracy of the bending levels to which they are coupled. On the basis of these considerations we adopt the model shown in Fig. 5.

The relaxation of CH_4 in the atmosphere is dominated by V-V transfer to O₂ and H₂O. The rate of transfer from CH_4 to O₂ is well documented, although it is not known whether it takes place from the near-resonant (0100) level or the infrared active (0001) level. Under the assumption that these levels are in equilibrium with each other we assign this process a room temperature rate equal to 6×10^{-13} cm³/s in

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the exothermic direction (O₂ transfer to CH₄). The reverse rate is obtained by detailed balance, using the partition function of the combined CH₄ (0001) and CH₄ (0101) levels. To scale this rate to higher levels we use the harmonic oscillator rule, as before. To scale this rate to different temperatures we assume that the reaction is sufficiently near resonance for the probability per collision to vary as T⁻¹. The rate coefficient in this

The rate of V-V transfer to $H_2O(\nu_2)$ is not so well documented, and there is some controver'y regarding the extraction of a large number of rate coefficients from the limited data on CH_4/H_2O mixtures. If we accept Bauer's interpretation of the data, the rate of transfer from H_2O (010) to $CH_4(\nu_2 + \nu_4)$ is 6×10^{-11} cm³/s at room temperature. To scale this rate to higher levels the harmonic oscillator rule is used, as before. To scale the rate to other temperatures we assume that the reaction is sufficiently near resonance that the rate varies as $T^{-1/2}$, as was assumed for transfer to O₂. The subsequent relaxation of $H_2O(\nu_2)$ and O₂ is discussed in

These processes are summarized in Fig. 5, where the relaxation times indicated correspond to the same atmospheric conditions as in Figs. 1 to 4. Only a very small amount of heating or cooling occurs at the absorption of a laser photon by CH4. At sufficiently low H2O concentrations ($\ll 0.2\%$) some significant cocling will occur on the fast time scale $(-4 \times 10^{-6} \text{s in Fig. 5})$ corresponding to transfer to O₂. Such small concentrations of H2O can occur at high altitudes, since H2O is not uniformly distributed throughout the atmosphere. Although V-V transfer from CH_4 (v2 and v4) to H2O(v2) is endothermic, this process will not lead to cooling because the H₂O(ν_2) vibration is quenched on the same time scale with a large release of heat. Thus, under conditions of sufficiently high humidity ($\gg 0.2\%$ H₂O), which ordinarily prevail at low altitudes, the laser energy absorbed by CH_4 will lead to heating on a fast time scale (~7 x 10-7s) corresponding to transfer to $H_2O(\nu_2)$ and quenching of the $H_2O(\nu_2)$ (principally by H₂O itself). The energy transferred to O₂ will appear as heat on a longer time scale (~10⁻⁴s) corresponding to the relaxation of O_2 via $H_2O(v_2)$.

F. KINETICS OF ABSORPTION BY HDO

HDO absorbs DF laser radiation on the v_1 fundamental transition

HDO
$$(000) + h\nu \rightarrow HDO (100) + \Delta E$$
. (19)

No data exist regarding the relaxation of HDO (v_1) (or v_2 or v_3 for that matter). However, pretiminary data have been obtained at AERL regarding the relaxation of $H_2O(v_1)$ in collisions with H_2O . These data indicate that modes v_1 and v_2 (and v_3 as well) are coupled at every H_2O-H_2O collision, despite the fact that the levels are separated by about 500 cm⁻¹. Because of the similarity of HDO to H_2O we assume that the upper levels of HDO (viz. (100), (020) and (001)) are closely coupled together with each other and with the corresponding levels of H_2O , as

-16-

indicated in Fig. 6. The relaxation of the "lumped levels" is then controlled by the relaxation of $H_2O(\nu_2)$, which is described in Section C, above.

The kinetics of HDO absorption are summarized in Fig. 6, where the times indicated correspond to the atmospheric conditions used in the previous figures. The dominant effect of absorption by HDO is rapid heating on a time scale of the order of 8×10^{-8} s, corresponding to quenching of $H_2O(v_2)$ by H_2O .



4

Fig. 6 Kinetics of HDO Absorption

-18-

IV. RESULTS

Figures 7-10 give the illustrative preliminary results for N_2O absorption at DF laser wavelengths. All cases assume a square wave 30 µsec pulse and 1 atm containing 0.3 ppm N_2O .

Figure 7 presents the translational temperature rise as a function of time during the pulse for each of the seven laser lines which are absorbed by N₂O. This represents a reasonable upper bound in that the incident power was taken as 10⁷ watts/cm² in the line and the water vapor concentration was high (20 torr). (The effect of water concentration on temperature rise is shown in Fig. 8.) Thermal effects after the power is shut off are not shown in Fig. 7. As is expected, the magnitude of the temperature rise is proportional to the N₂O absorption cross section with the largest ΔT for the laser line of the largest N₂O cross section.

Figure 8 shows the effect of H₂O concentration on the translational temperature rise. Because H₂O deactivates excited N₂O via a T-V process, the higher H₂O concentration results in more absorbed energy appearing as translational energy during the pulse. Twenty torr H₂O was chosen as a reasonable upper limit at sea level. Two torr is an unreasonable lower limit under expected conditions of interest and was chosen to illustrate a maximum effect of H₂O on temperature change and bleaching. (See Figs. 9 and 10)

Figures 9 and 10 show, for the laser line of largest N₂O absorption cross section, the power at 20 μ sec into vibration, temperature, transmission, absorption, and stimulated emission, all as a function of incident power for two H₂O concentrations. At all power levels the largest fraction of incident power is transmitted. When the change in net power absorbed (power absorbed minus stimulated emission) with increase in incident power approaches zero, the gas becomes "bleached" and any further increase in incident power results in no further increase in temperature. Bleaching occurs in Fig. 3 at an incident power level somewhere between 10' and 10⁸ watts/cm².

Comparison of Figs. 9 and 10 shows the effect of changing the H_2O concentration from 20 torr (Fig. 9) to 2 torr (Fig. 10). Decreasing the H_2O concentration results in less incident power going into temperature as was also shown in Fig. 8. A further result is bleaching at lower power levels as is evident in Fig. 10 where bleaching occurs at an incident power level between 10^6 and 10^7 watts/cm². Lower water concentrations decrease the rate of deactivation of excited N₂O which leads to bleaching at lower power levels.

The results presented above for N_2O absorption at DF laser wavelengths are preliminary, but sufficient to illustrate the magnitude of expected effects. Results for cases of operational interest for N_2O and the other absorbers at these wavelengths will be reported in the future as they become available.

1



Fig. 7 Translational Temperature Rise Due to N₂O Absorption of 7 DF Laser Lines



Fig. 8 Effect of Water Concentration on Temperature Rise for P₃(8) DF Line With N₂O Absorption







Fig. 10 Distribution of Power for Absorption by N_2O of the $P_3(8)$ DF Laser Line as a Function of Incident Power. $[H_2O] = 2$ Torr.

REFERENCES

- 1. T.F. Deutsch, Applied Phys. Letters, <u>10</u>, No. 8, p. 234, 15 April 1967.
- 2. N.G. Basov, et al., Applied Optics, <u>10</u>, No. 8, p. 1814, August 1971.
- 3. D. J. Spencer, et al., "Atmospheric Gas Absorption at DF Laser Wavelengths," Paper presented at "Absorption of Infrared Laser Radiation in the Atmosphere" Meeting, MITRE Corporation, April 1973.
- 4. R.A. McClatchey, et al., AFCRL Atmospheric Absorption Lane Parameters Compilation, Air Force Cambridge Research Laboratories, AFCRL-TR-73-0096, 26 January 1973.
- 5. B. H. Winters, et al., J. QSRT, <u>4</u>, p. 527 (1964).
- 6. David M. Bates, et al., "Line Parameters and Computer Spectra for Water Vapor Bands at 2.7 Microns," National Bureau of Standards Monograph 71, 3 August 1964.