EXPERIMENTAL CHECK ON A THEORETICAL MODEL FOR A CO_2 GDL BASED ON COMBUSTION PRODUCTS AT HIGH STAGNATION TEMPERATURES

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The working medium in a CO_2 GDL based on combustion products contains many components. The rapid advance in lasers of this type [1, 2] has been greatly facilitated by numerical calculations. A numerical model has been described [3-5] for a gasdynamic CO_2 laser based on the combustion products from C–H–O–N fuel, and a comparison has been made of the theoretical and measured weak-signal gains k_0 for stagnation temperatures of T_0 = 1100-1800°K/ the gain was chosen as the criterion because k_0 is simple and easy to measure and is one of the basic parameters of the active medium. It was found that in this range in T_0 the model with the rate constants selected for it is suitable for quantitative description of the characteristics of a CO_2 GDL with a compound working medium over fairly wide ranges in the stagnation pressure p_0, medium composition, and flow expansion conditions.

The efficiency of a CO_2 GDL increases with T_0 at least up to 2500°K [1, 2, 6], and it is therefore necessary to perform calculations on the laser characteristics at high T_0 over a wide range of compositions. The reliability of such calculations has to be examined. The equations for the vibrational energy-transfer kinetics given in [3] are applicalbe also at 1800-2500°K, since the lower vibrational levels of the molecules are mainly populated. However, many of the vibrational energy-transfer rate constants used in [3-5], in particular those for the rates of deactivation of the upper and lower laser levels of CO_2, have been measured at 300-1000°K and extrapolated to higher temperatures. The variation of many of the rate constants at high T_0 has little effect on the theoretical gain [4, 7] probably because the vibrational temperatures for the flow in the transonic region are initially close to the translational temperature, but then there is a rapid fall in the flow temperature, while the change in the stock of vibrational energy in the nitrogen is usually small within a short period (it is the less the narrower the neck and the larger the angle of the nozzle; such conditions are characteristic of profiled nozzles of minimal length with large degrees of flow expansion A/A_* as used at high T_0). A population usually begins to arise at a translational temperature much less than T_0. To obtain the correct result it is necessary for the rate constants to provide equilibrium between the vibrational and translational degrees of freedom at high flow temperatures, and they have to have reasonably reliable values during the formulation of the population inversion. A final answer to this question can come from comparing theory with experiment, which is the purpose of the present study.

A detailed comparison has been made [7, 8] of numerical models for the vibrational kinetics analogous to that described in [3-5], and good agreement was obtained over the calculated and measured k_0 at high T_0. However, in [7] the flow was that of a ternary mixture of CO_2, N_2, and H_2O through a slot, while in [8] the mixture consisted of CO_2, N_2, H_2O, and O_2 flowing hrough a wedge nozzle with a relatively high throat and a small angle, i.e., under expansion conditions of little practical interest. This was responsible for the low gains found in [8]. Therefore, the results of [7, 8] do not allow one to draw conclusions on the reliability in calculations on CO_2 GDL using combustion products at high T_0.

The literature shows that there have so far been virtually no measurements of k_0 at $T_0 > 1800$°K with the expansion conditions for complex media required for this case; there is only [9], but in it the media consisted largely of CO_2, N_2, H_2O, and O_2, but the profiled nozzles had degrees of expansion insufficiently large for high T_0.

We have measured and calculated k_0 for stagnation temperatures up to 2400°K for a series of multicomponent media covering almost all the limiting cases of working media for

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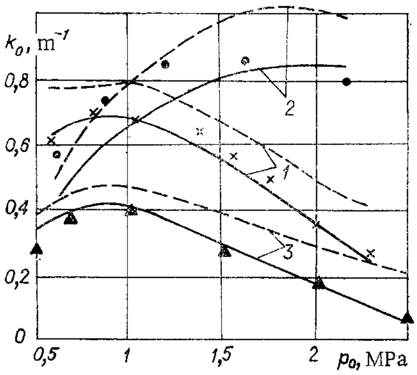

Fig. 1

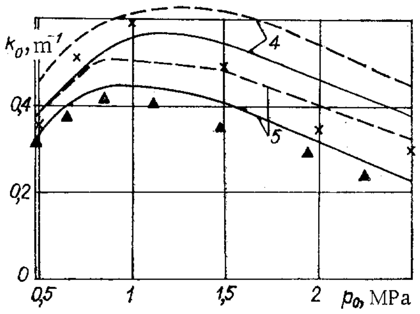

Fig. 2

CO_2 GDL based on combustion products, and we examined the flow through a profiled nozzle with a fairly large degree of expansion.

1. The experiments were performed with a GDL apparatus working in the quasistationary state [4, 5, 10-12]. Combustion under isochore conditions was used with model fuel mixtures composed of C_2H_2, H_2, CO, O_2, N_2O, CO_2, N_2 [11] to obtain hot working media with given compositions and temperatures. The maximum temperatures T_{max} attained by burning these mixtures in a chamber were calculated from the measured maximum pressure. After the membrane separating the combustion chamber from the nozzle unit ruptured, the combustion products expanded through a planar profiled nozzle of minimum length (with a nodal point) having a height of the throat $h = 3 \cdot 10^{-4}$ m, $A/A_* = 50$, and a width of 0.4 m. The active media were probed at a distance of 0.053 m down the flow from the throat using a continuous-wave electric-discharge laser working on P18 transition in the 00°1-10°0 band of CO_2. In each experiment we recorded the dependence of k_0 on p_0 and T_0, which varied adiabatically as the medium flowed from the combustion chamber. This enabled us to find T_0 from the known p_0. The heat transfer to the walls of the combustion chamber cannot be neglected at high T_0 and was allowed for by increasing the effective adiabatic parameter by a factor $1 + (S/S_*)St$ [13], where S and S_* are the areas of the heat-transfer surface and the critical section of the nozzle, while St is the Stanton number. Figures 1 and 2 show measured k_0 (in Fig. 1, the crosses show k_0 obtained in experiment 1, and the circles those in experiment 2, while the triangles relate to experiment 3; the crosses in Fig. 2 show k_0 obtained in experiment 4, and the triangles those in experiment 5). Table 1 gives the compositions of the model fuel mixtures (in mole %), the initial pressures p_i in the chamber before ignition, and the temperatures T_c and T_{max} obtained from thermodynamic calculations for the combustion of the mixture under isochore conditions. The stagnation parameters and the equilibrium compositions (in mole %) at the instants of measurement of k_0 are given in Table 2. We see that the composition of the combustion products varied little in each experiment. The working media obtained in experiments 2-5 contained correspondingly more N_2, H_2O, CO, O_2 by comparison with the medium in experiment 1.

The overall error in measuring k_0 was about 0.1 m^{-1} at all levels. The error in measuring p_0 was not more than 5%, but there was 10% error in determining T_0.

2. The calculation method has been described [3-5].† The calculations were performed for $T_0 < 2500$°K, so chemical processes in the flow were neglected [3, 5]. NO and OH occur

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†The V—T relaxation in the water vapor was incorporated in all the calculations.

TABLE 1

Experiment No.	C_2H_2	H_2	CO	O_2	N_2O	CO_2	N_2	$p_i \cdot 10^{-5}$, Pa	T_c, K	T_{max}, K
1	5,0	—	3,6	10,2	—	6,3	74,9	4,1	2500	2500
2	2,2	—	8,9	—	17,7	—	71,2	4,5	2150	2100
3	3,4	13,6	—	13,0	—	6,2	63,8	4,3	2500	2490
4	2,9	3,8	25,7	—	19,4	—	48,2	3,9	2500	2350
5	3,9	6,6	—	26,5	—	0,5	62,5	4,3	2500	2390

TABLE 2

Experiment No.	$p_0 \cdot 10^{-5}$, Pa	T_0, K	CO_2	H_2O	N_2	CO	O_2	NO	H_2	OH
1	23,0	2400	16,1	6,0	66,6	10,5	—	—	0,6	—
	20,3	2310	16,2	6,0	66,6	10,4	—	—	0,7	—
	17,7	2220	16,3	6,0	66,7	10,4	—	—	0,7	—
	15,5	2130	16,3	5,9	66,7	10,4	—	—	0,7	—
	13,7	2045	16,3	5,9	66,7	10,3	—	—	0,8	—
	10,5	1886	16,4	5,8	66,7	10,2	—	—	0,9	—
	8,0	1734	16,5	5,7	66,7	10,1	—	—	1,0	—
	6,2	1590	16,7	5,6	66,7	10,0	—	—	1,1	—
2	22,3	2000	10,7	2,0	85,1	2,1	—	—	0,1	—
	16,5	1800	10,7	2,0	85,1	2,0	—	—	0,1	—
	12,2	1640	10,7	2,0	85,1	2,0	—	—	0,1	—
	8,8	1480	10,8	2,0	85,1	2,0	—	—	0,2	—
	6,3	1320	10,8	1,9	85,1	1,9	—	—	0,2	—
3	25,3	2410	10,0	17,1	68,1	3,6	—	—	1,0	0,1
	20,3	2260	10,1	17,1	68,2	3,5	—	—	1,1	—
	15,2	2070	10,2	17,0	68,2	3,3	—	—	1,1	—
	10,1	1820	10,4	16,9	68,2	3,2	—	—	1,3	—
	7,1	1630	10,6	16,7	68,2	3,0	—	—	1,5	—
	5,1	1470	10,8	16,4	68,2	2,8	—	—	1,7	—
4	25,3	2345	8,3	4,4	63,8	21,4	—	—	2,0	—
	20,3	2197	8,4	4,3	63,8	21,4	—	—	2,1	—
	15,2	2020	8,6	4,2	63,8	21,2	—	—	2,2	—
	10,1	1796	8,8	3,9	63,8	21,0	—	—	2,4	—
	7,1	1626	9,1	3,7	63,8	20,7	—	—	2,7	—
	5,1	1468	9,4	3,4	63,8	20,4	—	—	3,0	—
5	22,7	2300	8,7	10,8	65,3	0,1	13,6	1,2	—	0,3
	19,8	2200	8,8	10,9	65,4	—	13,7	1,0	—	0,2
	15,0	2024	8,8	10,9	65,6	—	13,9	0,6	—	0,1
	11,3	1890	8,8	11,0	65,7	—	14,0	0,4	—	0,1
	8,6	1700	8,8	11,0	65,8	—	14,2	0,2	—	—
	6,5	1560	8,8	11,0	65,9	—	14,2	0,1	—	—
	4,9	1430	8,8	11,0	65,9	—	14;2	0,1	—	—

in the combustion products at high T_0, so additional vibrational relaxation channels were considered:

$$CO(1) + NO(0) \rightarrow CO(0) + NO(1); \tag{2.1}$$

$$N_2(1) + NO(0) \rightarrow N_2(0) + NO(1); \tag{2.2}$$

$$NO(1) + M \rightarrow NO(0) + M; \tag{2.3}$$

$$OH(1) + M \rightarrow OH(0) + M. \tag{2.4}$$

The calculations were based on measured [14] vibrational energy-transfer probabilities for channels (2.1) and (2.2):

$$p^{(2.1)} = \exp(1.7 \cdot 10^{-3} T - 9.7),$$

$$p^{(2.2)} = 10^{(3.8 \cdot 10^{-4} T - 4.14)}.$$

Here T is temperature, °K. The probabilities of V–T relaxation were calculated from the Schwarz–Slavskii–Herzfeld theory [15]. The solid lines in Figs. 1 and 2 show the calculated gains. In all cases there is good agreement with experiment.

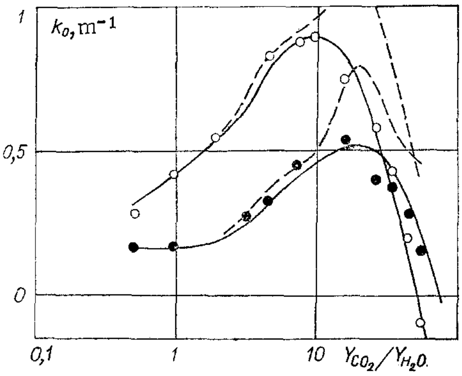

Fig. 3

3. In [8] we find rate constants $k^{(i)}$ different from those used above for vibrational relaxation channels important to a CO_2 GDL:

$$N_2(1) + H_2O \rightarrow N_2(0) + H_2O; \tag{3.1}$$

$$CO_2(00^01) + H_2O \rightarrow \begin{cases} CO_2(11^10) + H_2O; \\ CO_2(03^10) + H_2O; \end{cases} \tag{3.2}$$

$$CO_2(01^10) + H_2O \rightarrow CO_2(00^00) + H_2O. \tag{3.3}$$

The value of $k^{(3.1)}$ given in [8] is very low ($<3 \cdot 10^{-17}$ cm^3/sec), which appears to be due to a misprint; $k^{(3.3)} = 1.449 \cdot 10^6/T$ Pa^{-1}·sec^{-1} is too low at T > 600°K, while $k^{(3.2)} = 2.898 \cdot 10^2(1-\exp(-\theta/T))^3/[1-\exp(-\theta_3/T)$ Pa^{-1}·sec^{-1} is too low for T > 820 but too high for T < 800°K by comparison with the data of section 2 for the corresponding rate constants† (θ_2 and θ_3 in the expression for $k^{(3.2)}$ are the characteristic vibrational temperatures for the deformation and asymmetric modes of CO_2). Note that the values of $k^{(3.3)}$ from [8] correspond to the calculations of [16].

The calculations were performed with the values of $k^{(3.2)}$, $k^{(3.3)}$ from [8]; instead of the rate constants for (3.1) used in Sec. 2, we used the following dependence of $k^{(3.2)}$ on T:

$$k^{(3.1)} = \exp(4.29 - 28.78T^{-1/3})/[1 - \exp(-\theta_4/T)\,\mathrm{Pa}^{-1}\cdot\mathrm{sec}^{-1}. \tag{3.4}$$

Here θ_4 is the characteristic vibrational temperature of the nitrogen. The dependence of $k^{(3.1)}$ on T given by experimental studies [17-21] is close to that proposed in [21, 22].‡ It gives lower values $k^{(3.1)}$ at T $\geqslant$ 1000°K.

Initially, these rate constants are tested out on the results of experiments [24], which appear to be the most reliable. In these experiments, the dependence of k_0 on H_2O concentration was measured at distances of 0.063 and 0.143 m from the throat. The calculations were performed by $p_0 = 12.0 \cdot 10^5$ Pa, $T_0 = 1540$°K for the flow of a ternary mixture with a molar proportion of nitrogen $Y_{N_2} = 0.7$ through a profiled nozzle of minimum length with $h = 2.3 \cdot 10^{-4}$ m and $A/A_* = 30$. The broken line in Fig. 3 shows the results for k_0, while the filled and open circles show the values of k_0 found in [24] at distances of 0.143 and 0.063 m respectively. It is clear that at low H_2O concentrations ($Y_{CO_2}/Y_{H_2O} > 15$) the calculated values of k_0 are much larger than the measured ones. The reason for this lies in the values of $k^{(3.3)}$ at T < 800°K. For example, if we replace the T dependence of $k^{(3.3)}$ from [8] by that used in Sec. 2 [4, 5], while leaving the values of the other rate constants unchanged, we obtain good agreement with experiment, as in [4, 5] (solid lines in Fig. 3).

Therefore, for the comparison with the experimental results described in section 1 we used the values of $k^{(3.2)}$ from [8] in the calculations, with $k^{(3.1)}$ given by (3.4), while the other rate constants, including $k^{(3.2)}$, were as in Sec. 2. The broken lines in Figs. 1 and 2 show the resulting values for k_0. The agreement with experiment is then worse than before, particularly at T_0 = 1700-2400°K.

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† Curve 2 of Fig. 4 in [8] does not correspond to the data of [4] for the temperature dependence of $k^{(3.3)}$.

‡ In [22], a similar T dependence of $k^{(3.1)}$ is shown in Fig. 4, but the analytic expression given, which was then used in [2], does not correspond to this but describes the results given in [23].

Therefore, the rate constants for vibrational energy transfer used in Sec. 2 are suitable also for T_0 = 1800-2400°K, at least for the flow of a multicomponent working medium through a profiled nozzle with large A/A_* and small h. These rate constants give a better description of the relaxation in the flow than those considered in Sec. 3.

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