KINETICS OF CARBON DIOXIDE DISSOCIATION BEHIND A SHOCK FRONT

S. A. Losev and L. B. Terebenina

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 7, No. 4, pp. 133–138, 1966

ABSTRACT: The solution of a number of problems concerning the flow over or through bodies of a hot gas containing free or bound carbon and oxygen atoms requires a knowledge of the kinetics of the physicochemical processes in the oxides of carbon. This paper is devoted to an examination of the dissociation kinetics of carbon dioxide at high temperatures (up to 6000° K).

Several studies have been made of the kinetics of carbon dioxide dissociation; these include the work of Losev, Generalov, and Maksimenko [1] and the research of Brabbs, Belles, and Zlatarich [2]. In [1] the rate of dissociation of CO_2 molecules was measured at 3000–5500° K; in that study, however, the phenomena were analyzed only in the immediate vicinity of the shock front (about 3–4 mm), where dissociation has only just begun and the mole fraction of CO_2 is little different from unity. Only one direct dissociation reaction: $CO_2 + CO_2 \rightarrow CO + O + CO_2$, was taken into account; the role of the other possible reactions remained unclear. Brabbs and others [2] measured the dissociation rate of CO_2 in a mixture with argon at 2550–3000° K. These authors hypothesized dissociation of the CO_2 molecules through the ^3P excited electronic state with an energy close to the activation energy. Here, too, however, the possible contribution of other reactions to the CO_2 dissociation mechanism was not analyzed. Numerous studies have been devoted to the kinetics of the opposite process-combustion of carbon monoxide with the formation of carbon dioxide; nevertheless, it is still not possible to draw from these studies any definite conclusion about the mechanism and rate of the processes of formation and dissociation of carbon dioxide.

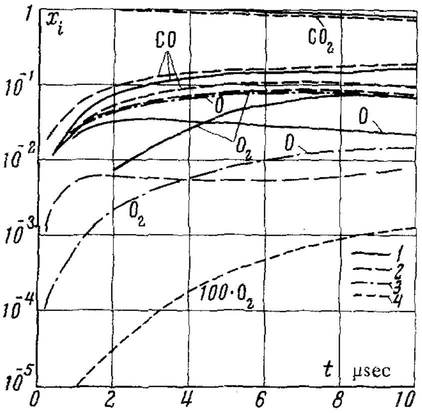

Fig. 1. Mole fractions of components behind a shock front in carbon dioxide (T_0 = 4450° K, p = 0.188 atm) at different values of k_2 (1–α_2 = = 1; 2–α_2 = 10; 3–α_2 = 0.1; 4–α_2 = 0). This figure contains an error: the lower curve 2 for the mole fraction of CO should have been a curve of type 4 corresponding to α_2 = 0; the second curve from the bottom (curve 2) corresponds to the mole fraction of O at α_2 = 10.

1. Formulation of the problem. We will consider the problem of the dissociation of molecules in the flow behind a shock from propagating in pure carbon dioxide gas. The final aim in solving this problem is to find the distribution of the thermodynamic characteristics and concentrations of the components of the gas in the flow behind the shock front. This permits a comparison with the experimental results and an estimation of the reliability of the assumptions. We assume that, behind the shock front, equilibrium is very rapidly established with respect to all the internal degrees of freedom of the CO_2 molecules and that then the process of dissociation beings, accompanied by the following reactions:

$$CO_2 + CO_2 \underset{k_1'}{\overset{k_1}{\rightleftarrows}} CO + O + CO_2, \tag{1.1}$$

$$CO_2 + O \underset{k_2'}{\overset{k_2}{\rightleftarrows}} CO + O_2, \tag{1.2}$$

$$O_2 + M \underset{k_3'}{\overset{k_3}{\rightleftarrows}} O + O + M, \tag{1.3}$$

where k_j and k_j' are the rate constants of the forward and reverse reactions.

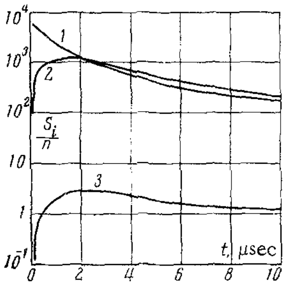

Fig. 2. Specific rates of reactions (1.1)–(1.3) behind a shock front in CO_2 (T_0 = 4380° K, p = 0.188 atm; $\alpha_1 = \alpha_2$ = 1).

For a one-dimensional steady-state flow the kinetic equations for the total change in the concentration of the i-th component in time (as a result of chemical reactions and change in gas density) take the form [3]

$$\frac{dn_i}{dt} = \left(\frac{dn_i}{dt}\right)_* - \frac{n_i}{v}\frac{dv}{dt}, \qquad \left(\frac{dn_i}{dt}\right)_* = (K_i)_*. \tag{1.4}$$

Here and in what follows $(K_i)_*$ relates to the change in concentration due to chemical reactions. We make use of the relations

$$\rho = \sum_i \mu_i n_i, \qquad \mu = \sum_i \mu_i x_i \qquad \left(x_i = \frac{n_i}{n} = \frac{p_i}{p}\right), \tag{1.5}$$

$$\frac{1}{v}\frac{dv}{dt} = -\frac{1}{\rho}\frac{d\rho}{dt}, \qquad \frac{dn_i}{dt} = n\frac{dx_i}{dt} + x_i\frac{dn}{dt}. \tag{1.6}$$

Here x_i is the mole fraction of the i-th component. We write Eq. (1.4) in the form

$$\frac{1}{n}(K_i)_* = \frac{dx_i}{dt} - \frac{x_i}{\mu}\sum_i \mu_i \frac{dx_i}{dt}. \tag{1.7}$$

We then write the relations for the laws of conservation of mass, momentum and energy for the gas behind the shock front for a one-dimensional steady-state flow without allowance for viscosity, heat conductivity and diffusion:

$$\rho_1 V = \rho v, \qquad p_1 + \rho_1 V^2 = p + \rho v^2, \qquad H_1 + {}^1\!/_2 V^2 = H + {}^1\!/_2 v^2, \tag{1.8}$$

the equation of state and Dalton's law:

$$p = \frac{\rho RT}{\mu}, \qquad p = \sum_i p_i, \tag{1.9}$$

and the equation expressing the constancy of the ratio of the number of carbon atoms to the number of oxygen atoms per unit volume:

$$\frac{n_1 + n_2}{2n_1 + n_2 + 2n_3 + n_4} = \frac{1}{2}. \tag{1.10}$$

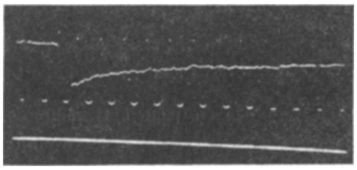

Fig. 3. UV absorption oscillogram (λ = 3000 A) for a shock wave in CO_2 (T_0 = 3810° K, p = 1.22 atm).

Here, the subscripts 1, 2, 3, 4 correspond to the components CO_2, CO, O_2, and O.

In this problem the other components are not considered, since at T < 6000° K in pure carbon dioxide they are present behind the shock front only in very low concentrations. Relations (1.9) and (1.10) enable us to express x_2 and x_4 in terms of x_1 and x_3:

$$x_2 = {}^1/_2\ (1 - x_1 + x_3), \qquad x_4 = {}^1/_2\ (1 - x_1 - 3x_3). \tag{1.11}$$

Then the molecular weight of the mixture

$$\mu = {}^1/_2\ \mu_1\ (1 + x_1 + x_3).$$

The specific rate of change of concentration $n^{-1}(K_i)_*$ depends on the specific rates S_j of the reactions (1.1)–(1.3); thus, for CO_2 and O_2

$$n^{-1}\ (K_1)_* = S_1 - S_2, \qquad n^{-1}\ (K_3)_* = S_2 - S_3, \tag{1.12}$$

where

$$S_1 = \frac{1}{n}(-k_1 n_1^2 + k_1' n_1 n_2 n_4) = \left(\frac{p}{kT}\right) k_1 x_1 \left(x_1 - \frac{p}{R_{(1.1)}} x_2 x_4\right),$$

$$-S_2 = \frac{1}{n}(-k_2 n_1 n_4 + k_2' n_2 n_3) = -\left(\frac{p}{kT}\right) k_2 \left(x_1 x_4 - \frac{x_2 x_3}{R_{(1.2)}}\right),$$

$$-S_3 = \frac{1}{n}\left(-k_3 n_3 n + k_3' n_4^2 n\right) = -\left(\frac{p}{kT}\right) k_3 \left(x_3 - \frac{p}{R_{(1.3)}} x_4^2\right). \tag{1.13}$$

Thus, using the above relations, we can reduce the problem to the solution of a system of equations of the first order in x_1 and x_3:

$$\frac{dx_1}{dt} = (1 + x_1)(S_1 - S_2) + x_1 (S_2 - S_3), \tag{1.14}$$

$$\frac{dx_3}{dt} = (1 + x_3)(S_2 - S_3) + x_3 (S_1 - S_3). \tag{1.15}$$

One of the basic quantities entering into the right sides of these equations is the temperature of the gas T. Using the expression for the law of conservation of energy (1.8), and making certain simplifications, we can obtain for T an explicit expression in terms of the mole fractions x_1 and x_3 and the shock wave velocity V. The enthalpy of the gas entering into (1.8)

$$H = \frac{1}{\mu}\sum_i h_i x_i = \frac{1}{\mu}\left\{x_1 \left(h_1 - \frac{h_2 + h_2^\circ + h_4 + h_4^\circ}{2}\right) + \right.$$
$$\left. + x_3 \left(h_3 + \frac{h_2 + h_2^\circ - 3h_4 - 3h_4^\circ}{2}\right) + \frac{h_2 + h_2^\circ + h_4 + h_4^\circ}{2}\right\}. \tag{1.16}$$

Here h_i are the molar enthalpies of the components, h_2^0, h_4^0 is the molar enthalpy at absolute zero. With an error of from 1.5 to 4% the values of h_i in the region 2000–6000° K can be approximated by the linear temperature dependence

$$h_i = b_i T + a_i. \tag{1.17}$$

Then, introducing the quantity

$$C = {}^1/_2\ \mu_1 H_1 + {}^1/_2\ \mu_1 V^2\ [1 - (\rho_1/\rho)^2] \tag{1.18}$$

and using (1.8), we obtain

$$T = [2Cf^{-1}\ (1 + x_1 + x_3) - x_1\ (2a_1 - a_2 - a_4 - h_2^\circ -$$
$$- h_4^\circ) - x_3\ (2a_3 + a_2 - 3a_4 + h^\circ_2 - 3h^\circ_4) - (a_2 + a_4 +$$
$$+ h_2^\circ + h_4^\circ)] \times [b_2 + b_4 + x_1 (2b_1 - b_2 - b_4) + x_3 (2b_3 +$$
$$+ b_2 - 3b_4)]^{-1}, \tag{1.19}$$

where $f = 4.18 \cdot 10^7$ erg/cal is the mechanical equivalent of heat.

We will assume that the gas pressure in the nonequilibrium flow region varies only slightly (p ≈ const). The gas density is determined from the equation of state:

$$\rho = \frac{p\mu_1}{fRT}\,\frac{1 + x_1 + x_3}{2}. \tag{1.20}$$

Thus, in its final form the problem consists in solving the system of differential equations (1.14), (1.15) with account for relations (1.11), (1.13), (1.18), (1.19), expanding the right sides of these equations. As an initial condition we may assume that at the beginning of dissociation (t = 0) $x_1 = 1$, $x_3 = 0$.

2. Initial data. In order to carry out the calculation it is necessary to assign numerical values to a number of quantities. Most important are the rate constants k_1, k_2, k_3. For k_1 as a first approximation we can use the expression [1]

$$k_1 = \alpha_1 3 \cdot 10^7 \left(\frac{D_1}{RT}\right)^6 \sqrt{T} \exp\left(-\frac{D_1}{RT}\right) \text{cc/mole}\cdot\text{sec}. \tag{2.1}$$

The quantity k_2 is unknown. As a starting expression for k_2 we will use the relation obtained by V. N. Kondrat'ev by analyzing the rates of reactions with molecules of similar structure:

$$k_2 = \alpha_2 6 \cdot 10^{12} \exp\left(-\frac{35000}{RT}\right) \text{cc/mole}\cdot\text{sec}. \tag{2.2}$$

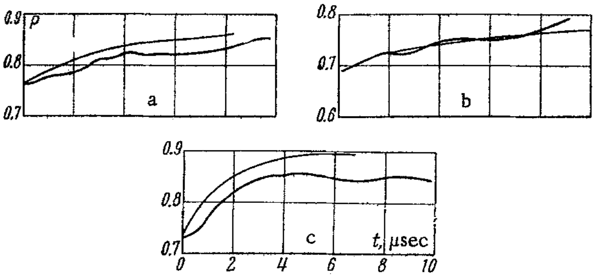

Fig. 4. Calculated (thin lines) and measured (thick lines) values of the distribution of transmittance P behind a shock front in CO_2 (a—T_0 = 3940° K, p = 0.635 atm; b—T_0 = 4120° K, p = 0.19 atm; c—T_0 = 4520° K, p = 1.04 atm).

The third reaction has been thoroughly studied and the constant k_3 is known with a sufficient degree of accuracy;* to be specific, we will take the k_3 for O_2–N_2 encounters:

$$k_3 = 2.5 \cdot 10^{11} \left(\frac{D_3}{RT}\right)^{1.5} \sqrt{T} \exp\left(\frac{D_3}{RT}\right) \text{cc/mole}\cdot\text{sec}. \tag{2.3}$$

---

*N. A. Generalov, Vibrational Excitation and Dissociation of Oxygen Molecules Behind a Shock Front [in Russian], dissertation, Moscow State University, 1963.

T_0, °K	p, atm	θ	T_0, °K	p, atm	θ	T_0, °K	p, atm	θ	T_0, °K	p, atm	θ
3300	0.872	10	4250	1.27	6.0	3920	0.626	2.5	4500	0.447	0.7
3420	1.398	10	4300	0.457	2.8	3940	0.635	2.4	4520	1.040	2.3
3420	0.892	4.0	4370	0.478	2.6	4030	0.958	6.0	4580	0.228	0.38
3440	1.534	3.5	4370	0.729	2.6	4050	0.907	2.6	4820	0.803	2.5
3560	0.985	3.2	4390	0.492	1	4120	0.178	2.4	5180	0.245	1.5
3800	1.017	5.0	4450	0.188	1.5	4120	0.190	1	5570	0.287	0.65
						4120	1.007	2.2	5660	0.233	2.2
						4160	0.680	4.0			

Here D_1 and D_3 are the energies of dissociation of CO_2 (into CO and O) and O_2, respectively. The factors α_1 and α_2 have been introduced into (2.1) and (2.2) owing to the need to vary these quantities.

The equilibrium constants for reactions (1.1)–(1.3) were computed from the equilibrium constants of the reactions $CO_2 = CO + (1/2)\,O_2 \cdot$ $\cdot R''_{(1.1)}$, $O_2 = 2O(R_{(1.3)})$, taken from tables [4]:

$$R_{(1.1)} = R'_{(1.1)}\sqrt{R_{(1.3)}}, \qquad R_{(1.2)} = \frac{R'_{(1.1)}}{\sqrt{R_{(1.3)}}}. \tag{2.4}$$

For $R'_{(1.1)}$ and $R_{(1.3)}$ we selected analytic relations of the type:

$$\lg R'_{(1.1)} = \frac{a}{T} + b, \qquad \lg R_{(1.3)} = \frac{c}{T} + d \tag{2.5}$$

where $a = 1.437 \cdot 10^4$, $b = 4.305$, $c = -0.267 \cdot 10^5$, $d = 6.989$. In the region $2000 < T < 6000°$ K the values thus obtained do not differ from the tabulated values by more than 15%, which is quite satisfactory.

For the molar enthalpy of the components, in accordance with (1.17), we took the values (cal/mole)

$$h_1 = 14.687T - 5280, \qquad h_3 = 9.301\,T - 2378,$$
$$h_2 = 8.795\,T - 1956, \qquad h_4 = 4.986\,T + 172. \tag{2.6}$$

and also $h_2^0 = 66\,770$ cal/mole, $h_4^0 = 58\,970$ cal/mole.

To carry out the calculation it is necessary to assign the shock wave velocity and the initial values of the temperature before the beginning of dissociation T_0 and the pressure p. These values are found with the help of (1.8) assuming equilibrium excitation of vibrations of the CO_2 molecules and the absence of dissociation (for given values of the shock wave velocity and the conditions ahead of the shock front).

3. Solution of the problem. The solution was obtained with the help of a computer. The computations were performed by the Runge-Kutta method in accordance with a standard program. The problem was solved with a constant time step $\Delta t = 2 \cdot 10^{-6}$ sec. A check showed that a tenfold reduction in the step has no effect on the result of integration. The calculation was terminated when the temperature difference between neighboring points was 5°. Altogether we calculated 30 different combinations of shock wave velocity and gas pressure; in some cases the values of α_1 and α_2 were varied.

The results of the calculations may conveniently be represented in a laboratory coordinate system, when the gas ahead of the shock front is at rest. For this purpose it is necessary to convert to the time reading t^0 in the laboratory system by means of the relation

$$t^0 = \int_0^t \frac{\rho_1}{\rho}\,dt. \tag{3.1}$$

Values of t^0 were also computed at the same time as the other quantities.

The calculations showed that, as in other cases of the development of relaxation processes behind a shock front, the gas temperature falls with distance from the front, while the density increases. The mole fraction of carbon dioxide gradually decreases, while the fraction of the other components increases. The mole fraction of carbon monoxide increases monotonically and amounts to about 10% after the first tenths of a μsec (in the laboratory reference system). At $\alpha_2 \geq 1$ the concentration of atomic oxygen has a maximum after 1–2 μsec (Fig. 1). With decrease in k_2 ($\alpha_2 = 0.1$, 0) the rate of formation and the mole fraction of O_2 fall sharply, since in this case molecular oxygen can only be formed as a result of the triple encounters O + O + M, whose probability is low. On the other hand, the mole fraction of O increases.

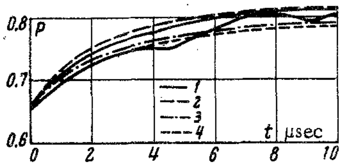

Fig. 5. Effect of rate of reaction (1.2) on transmittance ($T_0 = 5180°$ K, p = 0.245 atm); thin lines: $1-\alpha_2 = 1$; $2-\alpha_2 = 10$, $3-\alpha_2 = 0.1$; $4-\alpha_2 = 0$, thick line—experiment.

At the very beginning the contribution of the first reaction of the specific dissociation rate considerably exceeds the contribution of the second and third reactions (for less than 1μsec). Then S_2 approaches and may even exceed S_1 (Fig. 2). The contribution of the third reaction is always relatively small. The reverse reaction rates are always less than the forward reaction rates; this difference is greatest for the first and third reactions involving triple encounters.

A comparison with experiment must be of decisive importance in estimating the reliability of the results obtained and selecting values of α_1 and α_2.

4. Experimental apparatus and results. The apparatus employed was similar to that used previously in [1]. The experiments were conducted in a stainless-steel shock tube with an inside diameter of 50 mm. To analyze the composition of the gas behind the shock front, we used the method of absorption spectral analysis in the UV region of the spectrum, where the hot gas has considerable absorptivity [6]. For this purpose we selected an optical system similar to that described in [6]. The carbon dioxide gas used in the experiments was dried by being passed through a coil cooled by a mixture of dry ice and acetone and through silica gel filters. Then the gas was fractionated by freezing with liquid nitrogen. This procedure gave sufficiently pure carbon dioxide with an impurity content which, as shown by mass spectrometry, did not exceed 0.1–0.01%. The shock wave velocity was measured correct to 1–2% by means of ionization probes.

The oscillograms obtained for the distribution of absorption along the flow behind the shock front at $\lambda = 3000$ Å have the form shown in Fig. 3. When the shock front arrives at the section in question, a sharp drop in the signal is observed—the excited CO_2 molecules begin to absorb light; then the absorption decreases (signal increases) as a result of the dissociation of CO_2.

5. Comparison of calculations and experiment. For purposes of comparison, in each case we calculated the transmittance P = 1 − − A (A is the absorptance), using the expression derived from Beer's law:

$$P = \exp\left(-\frac{lp}{k}\frac{\sigma(T)}{T}x_1\right).$$

The validity of this expression in our case was demonstrated in [5], where the temperature dependence of the absorption cross section σ(T) was also obtained. In computing P we took the values of x_1, T, and p obtained in solving the problem examined above. The value of l was taken equal to the diameter of the shock tube. Thus, the each variant we obtained a distribution of P as a function of time after passage of the shock front past the observation windows for initial conditions corresponding to the experimental conditions.

Typical calculated and experimental values of the distribution of transmittance P are given in Fig. 4 for three pairs of values of T_0 and p. On the whole, the agreement between theory and experiment is satisfactory (within one order with respect to time). To characterize the deviation of the calculated from the experimental values we introduce the quantity $\theta = (\Delta t^{*}/\Delta t^{**})$, where Δt^{*} and Δt^{**} are the times taken to reach the same transmittance levels in the experiments and in the calculations, respectively. For simplicity, we set $\Delta t^{**} = 1$ μsec. It was found that the calculated values (at $\alpha_1 = \alpha_2 = 1$) are particularly close to the experimental values ($\theta \sim 1$) at a pressure in the flow behind the shock front $p \leq 0.5$ atm; at higher pressures θ is several times greater than unity, i.e., the experiment is characterized by the slower establishment of equilibrium. This may indicate a transition to a monomolecular mechanism of dissociation of CO_2 at high pressures (lowering of the order of the reaction). However, this conclusion requires further study supported by experiments over a wider range of pressures.

We will consider the results of varying α_1 and α_2. The variation of α_1 showed that the dimensions of the nonequilibrium zone (and the entire pattern of distribution of the parameters in it) are almost inversely proportional to the reaction rate. Variation of α_2 has little effect on the distribution of x_1 and hence on the distribution of the transmittance P: changing α_2 by several orders and even taking $\alpha_2 = 0$ does not have much effect either on x_1 or on the value of P, as may be seen from Fig. 5, where $T_0 = 5180°$ K, $p = 0.245$ atm. Consequently, the measuring method employed does not permit determination of the quantity k_2 owing to the low sensitivity of P to changes in k_2. At the same time, a change in k_2 has an appreciable effect on the rate of formation of O_2 (see Fig. 1). It may be assumed that the quantity α_2 may be much less than unity and, in any event, does not exceed unity. For a more precise determination of k_2 it is necessary to make simultaneous measurements of the concentration distribution of some other component, in addition to CO_2.

6. Carbon dioxide dissociation kinetics. The above analysis makes it possible to sketch the following picture of the process of dissociation behind a shock front in pure carbon dioxide at a velocity $V \sim 3$–4 km/sec and a pressure behind the front close to atmospheric.

The dissociation of CO_2 begins with the reaction

$$CO_2 + CO_2 \rightarrow CO + O + CO_2;$$

then in a very short time (fractions of a microsecond) there is formed in the gas a number of oxygen atoms sufficient to sustain the second reaction

$$CO_2 + O \rightarrow CO + O_2.$$

After 2–3 μsec the rates of these reactions become practically equal, i.e., all the atomic oxygen reacts immediately with CO_2, and for all the rest of the process we can write the combined reaction

$$CO_2 + CO_2 \xrightarrow{k_{12}} 2CO + O_2. \qquad (6.1)$$

Thus, the role of the second reaction in the dissociation kinetics of CO_2 behind a shock front is a considerable one. On the other hand, under the conditions examined the role of the third reaction

$$O_2 + M \rightarrow O + O + M$$

is not very great.

Thus, taking into account only the one combined reaction (6.1) makes it possible to adopt the simplified assumption that after a few microseconds $x_4 \approx 0$.

The calculations confirmed the possibility of an experimental determination of the value of the rate constant of the first reaction at the very beginning of the nonequilibrium zone ($t \leq 1$ μsec) where the role of the second reaction is still small. This possibility was also realized in [1].

The authors thank E. B. Belyaev for assisting with the computer calculations.

REFERENCES

1. S. A. Losev, N. A. Generalov, and V. A. Maksimenko, "Study of the dissociation of CO_2 molecules at high temperatures," DAN SSSR, 150, no. 4, 839, 1963.

2. T. A. Brabbs, F. E. Belles, and S. A. Zlatarich, "Shock-tube study of carbon dioxide dissociation rate," J. Chem. Phys., vol. 38, no. 8, p. 1939, 1963.

3. J. O. Hirschfelder, S. Curtiss, and R. Bird, Molecular Theory of Gases and Liquids [Russian translation], IL, 1961.

4. Thermodynamic Properties of Individual Substances. A Handbook [in Russian], vol. II, Izd-vo AN SSSR, 1963.

5. N. A. Generalov, S. A. Losev, and V. A. Maksimenko, "Absorption of UV radiation by strongly heated CO_2," Optika i spektroskopiya, vol. 15, no. 1, p. 27, 1963.

30 November 1964 Moscow