

# Atomic Resonance Absorption Spectroscopy Measurements on High-Temperature CO Dissociation Kinetics

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The dissociation rate coefficient of CO was measured behind reflected shock waves in the temperature range  $5500 \leq T \leq 9000$  K. By the use of the atomic resonance absorption spectroscopy (ARAS), the time-dependent formation of C and O atoms could be directly observed in the postshock reaction zone. The experiments were performed in mixtures of CO highly diluted in argon at pressures between 0.5 and 1.3 bar. The initial CO concentrations varied from 100 to 10,000 ppm. Assuming vibrational equilibrium, the data for the thermal decomposition of CO,  $(\text{CO} + \text{Ar} \xrightarrow{k_1} \text{C} + \text{O} + \text{Ar})$ , can be represented by the following modified Arrhenius expression:  $k_1 = 4.3 \times 10^{27} T^{-3.1} \exp(-129,000 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \pm 50\%$ . Computer simulations based on a two-temperature model were not able to explain observed reaction induction times. Vibrational relaxation alone seems to have a negligible influence under the present conditions. The effect of impurities was minimized by keeping background pressure in the shock tube below  $5 \times 10^{-7}$  mbar.

## I. Introduction

THE high-temperature thermal dissociation of carbon monoxide



which is, for example, of interest in hypersonic flows over carbonaceous surfaces, has been studied in several shock tube experiments<sup>1-5</sup> and is part of theoretical considerations and reviews.<sup>6-9</sup> In nearly all papers, the bond dissociation temperature was assumed to be 129,000 K ( $D = 1072 \text{ kJ mole}^{-1}$ ). Apart from the work of Hanson,<sup>3</sup> who followed the end wall pressure and the  $\text{C}_2$  emission, all other experiments were done by measuring the CO concentration during the dissociation process. Appleton et al.<sup>1</sup> determined the rate coefficient based on vacuum uv absorption of CO, whereas Davies,<sup>2</sup> Chackerian,<sup>4</sup> and Presley et al.<sup>5</sup> measured the CO concentration by infrared emission spectroscopy. All of these investigations were summarized by Baulch et al.,<sup>8</sup> who recommend a rate coefficient for CO dissociation with  $M = \text{Ar}$  based on data from Davies<sup>2</sup> and Appleton et al.<sup>1</sup> In all of the experimental studies the reaction induction time seems to be longer than the extrapolated vibrational relaxation time. Fairbairn<sup>10,11</sup> and Appleton et al.<sup>1</sup> described the induction period and the following steady-state dissociation by a mechanism which included electronically excited CO and  $\text{C}_2$  as active intermediate species dissociating to the products C and O.

The aim of the present study is to determine the carbon monoxide dissociation rate coefficient by measuring the time-dependent concentrations of the reaction products C and O. The experiments were performed in the temperature range  $5500 \leq T \leq 9000$  K using atomic resonance absorption spectroscopy (ARAS) to measure the concentrations of the atomic species. In the past the combination of shock tube technology and ARAS proved to be a very sensitive and powerful technique for high-temperature gas phase kinetics studies.<sup>12-15</sup> To our knowledge it is the first time that the reaction products were measured during CO dissociation. Since the initial CO

was highly diluted in argon, the chemistry can be assumed to be decoupled from transport processes, and simple kinetic interpretation of the measured atom concentration is made possible.

## II. Experimental

The experiments were conducted behind reflected shock waves in a stainless-steel shock tube of 79 mm inner diameter. The tube is constructed as an ultrahigh vacuum apparatus and can be heated and evacuated through a special endplate valve using a forepump, a turbomolecular pump, and a liquid nitrogen-cooled titanium sublimation pump down to pressures of about  $5 \times 10^{-8}$  mbar. Typical rates of leaks plus outgassing were  $5 \times 10^{-6}$  mbar/min. A detailed description of the experimental setup is given in Refs. 12-14.

The CO/Ar mixtures were prepared in a stainless-steel cylinder by using the partial pressure method. The gas mixing setup can be heated and evacuated by a pump arrangement like the shock tube. Because of the high sensitivity of the ARAS detection technique, all gases used were of ultra-high purity: Ar 99.9999%; CO 99.997%. The initial concentrations of CO in argon varied between 100 and 10,000 ppm. Prior to each run the tube was evacuated to about  $5 \times 10^{-7}$  mbar or lower. It was filled with gas mixtures having initial pressures in the range  $2.0 \leq p \leq 7.5$  mbar. Diaphragms made of aluminum, 70  $\mu\text{m}$  thick, were ruptured by increasing the driver gas ( $\text{H}_2$ ) pressure. The temperature and pressure behind the reflected shock waves were computed from the measured incident shock speed using one-dimensional shock equations. The incident shock velocity was measured with the help of four thin film gauges (placed along the test section at known intervals) and a four-channel transient recorder having a storage capacity of 64 kbyte per channel and a sample time of 100 ns.

The optical detection technique used is a line emission-line absorption method. The arrangement consists of a microwave-excited discharge lamp, the absorption zone in the shock tube which is separated on both sides by two thin lithium fluoride windows, a 1-m McPherson vacuum uv monochromator and a special solar-blind photomultiplier. The corresponding spectral lines OI and CI were excited in gas mixtures of He with 1%  $\text{O}_2$  or  $\text{CO}_2$  which passed through the lamp at a pressure of 6 mbar. The ARAS technique was applied to measure O-atom concentrations at the OI triplet at 130.5 nm and C-atom concentrations at the CI quintet at 156.1 nm. Spectral shapes of the lines emitted by the resonance lamp are not known precisely as a result of self-absorption or perhaps self-reversal. Hence, a simple relation between

Received June 21, 1991; revision received Sept. 5, 1992; accepted for publication Sept. 5, 1992. Copyright © 1992 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved.

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the directly measured absorption and the atom concentrations does not exist. Therefore, a series of carefully controlled shock wave calibrations were conducted to relate the absorptions to the corresponding O- and C-atom concentrations. An example of the C-atom calibration is given in Ref. 16. In these experiments no significant temperature dependence of the C-atom absorption cross section was observed. For example, an absorption of 50% corresponds to a C-atom concentration of about  $2.9 \times 10^{13} \text{ cm}^{-3}$ . In the present experiments the C-atom measurements during CO dissociation were performed under very similar temperature conditions as compared to the calibration experiments.

For O atoms, the required relation between atom concentration and resulting absorption was obtained in shock-tube calibration experiments of  $\text{N}_2\text{O}/\text{Ar}$  mixtures. Under temperature conditions  $T > 2000 \text{ K}$  the initial reactant  $\text{N}_2\text{O}$  decomposes very rapidly and completely into  $\text{N}_2$  and O thus serving as an ideal O-atom source. The resulting absorption was measured and correlated with the O-atom concentration by the modified Lambert-Beer law using a concentration exponent of  $n = 0.8$ . The absorption cross section obtained is shown in Fig. 1. This result is valid for absorptions of  $0.15 \leq A \leq 0.85$ . As can be seen from Fig. 1, no significant temperature dependence of the absorption cross section was observed. The results can be presented by a mean value of

$$\sigma_{\text{OI}}(\text{O}) = 2.55 \times 10^{-12} \text{ cm}^2$$

which is valid for a temperature range  $5700 \leq T \leq 8900 \text{ K}$ . An absorption of 50% corresponds to an O-atom concentration of about  $1.5 \times 10^{13} \text{ cm}^{-3}$ .

### III. Results

The dissociation of CO was studied in the temperature range  $5500 \leq T \leq 9000 \text{ K}$  at pressures between 0.5 and 1.3 bar. In 18 shock tube experiments, the O-atom absorption was measured at initial CO concentrations between 100 and 10,000 ppm. C-atom absorption was measured in four experiments performed with initial CO concentrations from 2500 to 10,000 ppm. The conditions of all experiments carried out are listed in Table 1.

The temperature range for O-atom experiments is given by the detection limits of the ARAS method. The same is true for the low temperature side of C-atom measurements. The highest temperature of 5600 K used in the C-atom absorption experiments was limited by emission processes, which make the interpretation more complicated. Typical extinction signals obtained from individual shock tube experiments are shown in Fig. 2. In principle, both signals are composed of a time-independent part which is a result of absorption of the

Table 1 Experimental conditions and inferred rate coefficients

<i>T</i> , K	<i>p</i> , bar	[CO], ppm	<i>k</i> <sub>CO,M</sub> , cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
O-atom measurements			
7199	0.80	100	$8.80 \times 10^7$
7889	0.60		$3.48 \times 10^8$
8924	0.55		$2.12 \times 10^9$
6550	0.97	250	$1.88 \times 10^7$
7161	0.80		$9.83 \times 10^7$
8169	0.62		$8.92 \times 10^8$
6504	0.96	500	$1.42 \times 10^7$
7168	0.80		$9.14 \times 10^7$
8174	0.62		$8.62 \times 10^8$
6435	0.95	1000	$1.81 \times 10^7$
6996	0.78		$4.57 \times 10^7$
8194	0.62		$6.70 \times 10^8$
6392	0.94	2500	$1.80 \times 10^7$
8236	0.62		$4.71 \times 10^8$
5705	1.24	5000	$1.46 \times 10^6$
6466	0.96		$2.01 \times 10^7$
5626	1.22	10,000	$3.20 \times 10^6$
6461	0.95		$1.80 \times 10^7$
C-atom measurements			
5630	1.13	2500	$2.12 \times 10^6$
5607	1.21	5000	$1.47 \times 10^6$
5732	1.15		$1.74 \times 10^6$
5596	1.21	10,000	$1.26 \times 10^6$

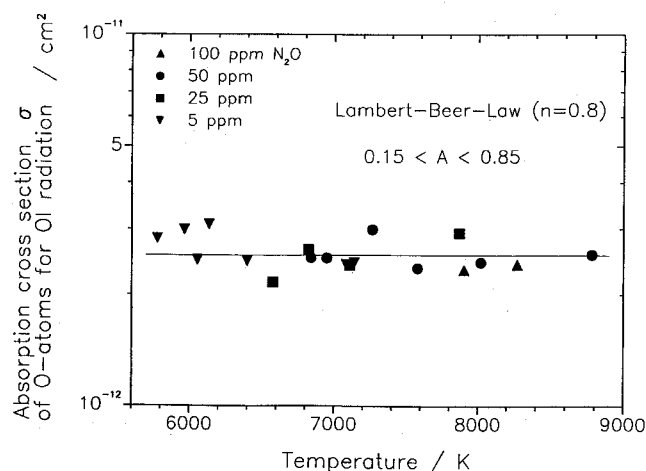


Fig. 1 Absorption cross section of O atoms for OI radiation at 130.5 nm determined from  $\text{N}_2\text{O}/\text{Ar}$  experiments.

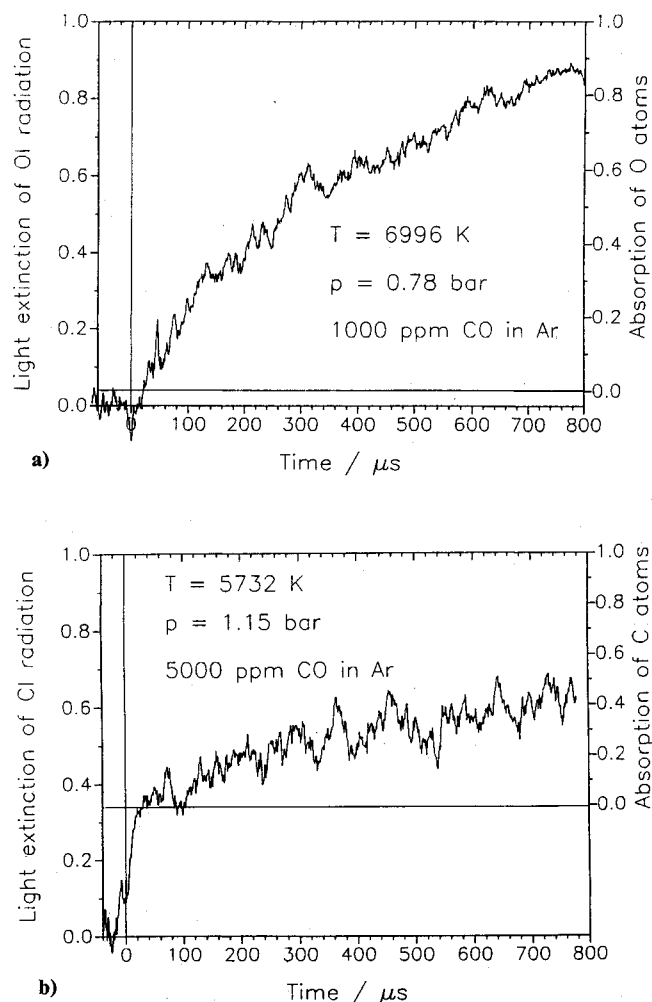


Fig. 2 Light absorption measurements of two individual experiments, a) O-atom absorption and b) C-atom absorption.

initial reactant CO and a time-dependent part caused by absorption of the atomic species C and O, respectively. To evaluate the measured extinction signals in terms of atomic concentrations it is necessary to know the absorption cross section of CO for OI and CI radiation. In a series of lower temperature shock tube experiments, the absorption cross section of CO for CI radiation, defined by the Lambert-Beer law, was determined. From the rapid signal increase behind the reflected shock wave, which is a result of CO absorption, a value independent of temperature and concentration of

$$\sigma_{\text{CI}}(\text{CO}) = 1.2 \times 10^{-17} \text{ cm}^2$$

was obtained. The absorption of OI radiation by CO was measured in the temperature range  $4000 \leq T \leq 5600$  K. The absorption cross section obtained decreases with increasing initial CO concentration of 100 ppm to 10,000 ppm, whereas the temperature effect was negligible. Values of

$$\sigma_{\text{OI}}(\text{CO}) = 4.0 \times 10^{-18} - 1.0 \times 10^{-17} \text{ cm}^2$$

are comparable with results of Thielen and Roth,<sup>15</sup> who found an absorption cross section with similar temperature and concentration dependence. The extrapolation of their values into our temperature range agrees very well with the present measurements.

Using the O- and C-atom calibration curves and the absorption cross sections of CO, all of the extinction signals mea-

Table 2 Reaction mechanism for the sensitivity analysis

Reaction	<i>A</i>	<i>n</i>	<i>E<sub>a</sub></i>	Ref.
R1 CO + Ar → C + O + Ar	$4.30 \times 10^{27}$	-3.1	129,000	This study
R2 C + CO + Ar → C2O + Ar	$2.29 \times 10^{16}$			21
R3 CO2 + Ar → CO + O + Ar	$3.89 \times 10^{14}$		53,980	21
R4 O2 + Ar → O + O + Ar	$1.80 \times 10^{18}$	-1.0	59,470	21
R5 C2 + Ar → C + C + Ar	$3.72 \times 10^{14}$		69,870	21
R6 CO + O2 → CO2 + O	$5.06 \times 10^{13}$		31,820	21
R7 C + O2 → CO + O	$1.20 \times 10^{14}$		2,010	21
R8 C2 + O → CO + C	$3.00 \times 10^{14}$			11

$k = A \times T^n \exp(-E_a/T)$ ; units for *k*: cm, mol, s.

sured can easily be transformed into O- and C-atom concentration profiles. Typical individual examples are shown in the upper and lower parts of Fig. 3. The experimental uncertainties of the atom concentrations are on the order of  $\pm 25\%$ . Under the present conditions, both O- and C-atom concentrations increase in all of the cases linearly with time, showing short induction time.

#### IV. Discussion

The interpretation of the measured O- and C-atom formation during thermal dissociation of CO was performed by using a kinetic system of eight elementary reactions presented in Table 2. A sensitivity analysis of this system with respect to the atomic species was done using the SENKIN program code from Sandia National Laboratories.<sup>17</sup> As a result, Fig. 4 shows the normalized sensitivity

$$S_{X,j} = \frac{A_j}{[X]} \cdot \frac{\partial [X]}{\partial A_j}, \quad X = \text{C or O} \quad (1)$$

of the four most important reactions for typical experimental conditions. *A<sub>j</sub>* is the pre-exponential factor of the rate coefficient of reaction *j*. For both O as well as C atoms the highest sensitivity is going to reaction (R1), what is an expected result. Compared to (R1) the influence of the other reactions of Table 2 on the C- and O-atom profiles is negligible, particularly at early reaction times. Consequently, the reaction



was assumed to be the only relevant reaction during CO dissociation under our experimental conditions. Because of the comparable collision efficiencies of CO and Ar and the high dilution of CO, the collision partner *M* was set equal to Ar. From the dissociation reaction (R1), the rate coefficient can be related to the rate of change of the reaction products O and C

$$k_{\text{CO,Ar}} = \frac{d[\text{O}]/dt}{[\text{CO}]_0[\text{Ar}]} = \frac{d[\text{C}]/dt}{[\text{CO}]_0[\text{Ar}]} \bigg|_{t > 20 \mu\text{s}} \quad (2)$$

The results of the 18 O-atom and 4 C-atom experiments are listed in Table 1 together with the detailed experimental conditions. The temperatures given there are equilibrium values calculated on the basis of the measured shock speed. The rate coefficients obtained are summarized in the Arrhenius diagram of Fig. 5. Both the O- and the C-atom measurements show consistent results for the rate coefficient *k<sub>CO,Ar</sub>*. Using the well-established dissociation energy (temperature) of CO, the experimental results can be represented by the following modified Arrhenius expression,

$$k_{\text{CO,Ar}} = 4.3 \times 10^{27} T^{-3.1} \exp(-129,000 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (3)$$

shown as solid line in Fig. 5. The standard deviation due to experimental scatter is about  $\pm 30\%$ . The combined uncertainty from the calibration procedure and the experimental scatter is about  $\pm 50\%$ .

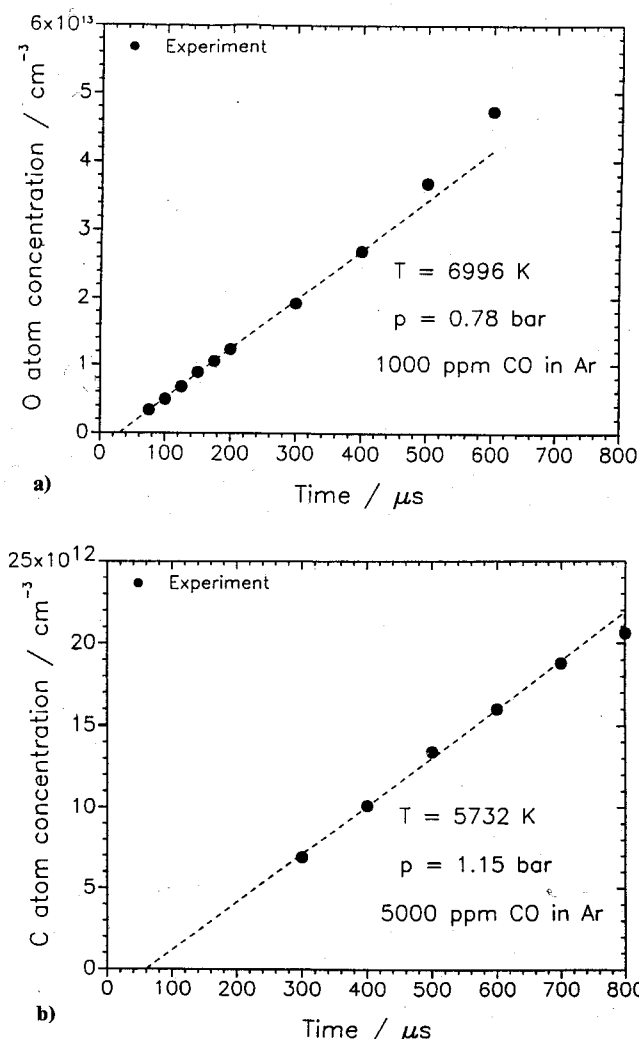


Fig. 3 Atom concentration measurements during thermal decomposition of CO, a) O atoms and b) C atoms.

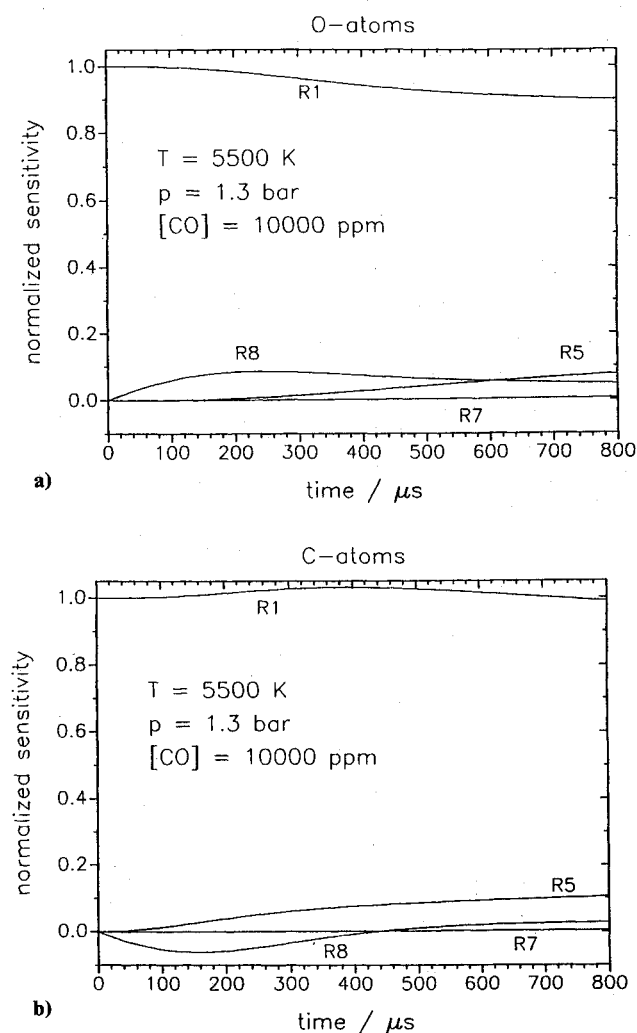


Fig. 4 Normalized sensitivity for the most important reactions of the system given in Table 2, a) with respect to O atoms and b) with respect to C atoms.

During the present experiments an induction behavior for the appearance of the atomic species O and C was observed. We have determined the corresponding induction time from the experimental concentration profiles in the normal way by calculating the interval between the time corresponding to the crossing of the steepest slope line with the concentration base line and the arrival time of the reflected shock wave. According to Appleton et al.<sup>1</sup> the resulting data can be presented as an induction coefficient  $(\tau^2[\text{CO}][M])^{-1}$ . Results obtained are shown in Fig. 6 together with the induction coefficient for the disappearance of CO after Ref. 1 and the vibrational relaxation coefficient of CO calculated with the data of Hooker and Millikan.<sup>18</sup> It is obvious that the temperature dependence of all three induction coefficients is nearly identical, but the absolute values differ significantly. The measured induction coefficient for the appearance of O atoms is a factor of about 4000 smaller than the vibrational relaxation coefficient of CO but a factor of about 250 higher than the induction coefficient of Ref. 1 for the disappearance of CO.

Appleton et al.<sup>1</sup> have tried to explain their difference between reaction induction time and vibrational relaxation time by vibrationally and electronically excited states of CO and intermediate chemical species. The significantly shorter reaction induction time determined in this study, which is compared to Ref. 1 closer to the vibrational relaxation time of the initial reactant, seems to be a result of the higher detection sensitivity compared to the work of Appleton et al.<sup>1</sup> In their experiments they determined changes in the concentration of the initial reactant CO on a high concentration level, whereas

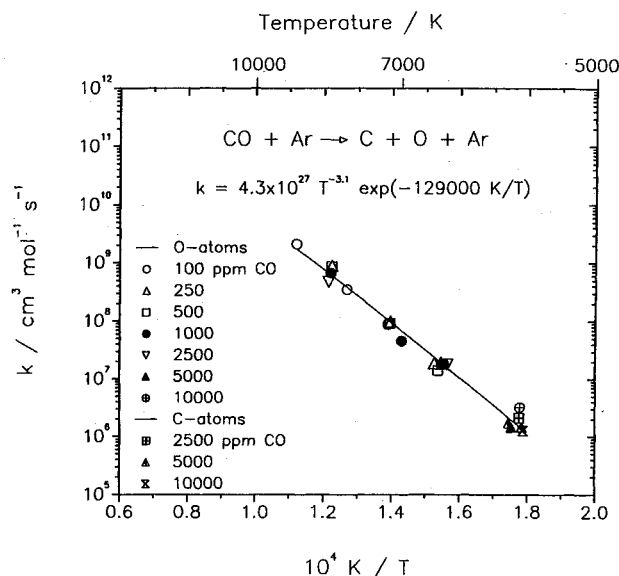


Fig. 5 Arrhenius representation of the present rate coefficient for the thermal decomposition of CO.

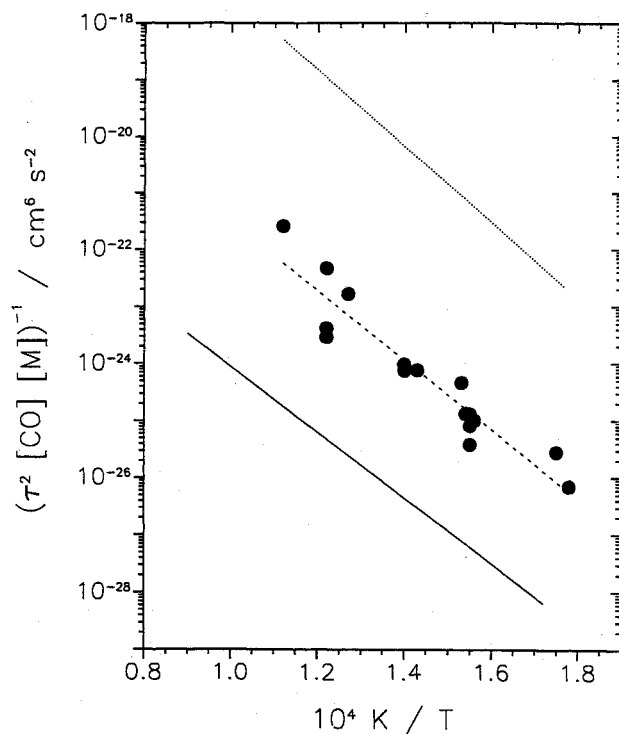
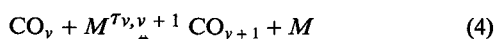


Fig. 6 Induction time  $\tau$  represented as induction coefficient  $(\tau^2[\text{CO}][M])^{-1}$ : — induction time for the disappearance of CO molecules measured by Appleton et al.<sup>1</sup>, • induction time for the appearance of O atoms from the present study, and ... vibrational relaxation time for CO calculated with the data of Hooker and Millikan.<sup>18</sup>

in our study changes in the product concentrations were measured with high sensitivity on a zero base level.

The difference between the measured reaction induction time and the vibrational relaxation in coupled processes of vibrational excitation and thermal decomposition is a known phenomenon, see Boyd and Burns.<sup>19</sup> In the present case the coupling between vibrational relaxation and thermal dissociation was described by a two-temperature model to demonstrate the influence of the vibrational relaxation process on the dissociation rate under our experimental conditions. It includes vibrational relaxation of CO assuming partial vibrational equilibrium characterized by the vibrational temperature, and vi-

brational-selective dissociation of CO by collisions with a partner  $M$ .



In these equations  $\text{CO}_v$  corresponds to the number density of CO in the vibrational state  $v$ , whereas  $\tau_{v,v+1}$  and  $k_v$  are the relaxation time for the indicated vibrational transition and the dissociation rate coefficient of the respective vibrational level. For the two sets of rate parameters the following relations were introduced:

$$\tau_{v,v+1} = [\tau_{0,1}/(v+1)] \quad (6)$$

$$k_v = k_{\text{CO,Ar}}(T) \exp\left(\frac{v\theta_{\text{vib}}}{T}\right) \quad (7)$$

Equation (6) is valid for harmonic oscillators, see Heims,<sup>20</sup> which relax through a series of Boltzmann distributions characterized by the vibrational temperature  $T_{\text{vib}}$ . In this case the whole process is determined by one rate parameter  $\tau_{0,1}$  of the ground state vibrational transition. The vibrational selective rate coefficient  $k_v$  of Eq. (7) was assumed to be dependent on the rate coefficient  $k_{\text{CO,Ar}}$  of the ground state level ( $v=0$ ) corrected by the given exponential expression which contains the characteristic vibrational temperature  $\theta_{\text{vib}}$ . It expresses the fact that the activation temperature of  $k_v$  decreases with increasing quantum number  $v$ .

The coupling between vibrational relaxation and dissociation of CO behind shock waves was simulated based on a model including 11 vibrational levels ( $v=0-10$ ) of CO using the described mechanism. The remaining two rate parameters in Eqs. (6) and (7) were assumed according to Hooker and Millikan<sup>18</sup> for  $\tau_{0,1}$  and to Eq. (3) of this paper for  $k_{\text{CO,Ar}}$ . The post shock initial conditions were calculated from the one-dimensional shock wave conservation equations assuming frozen vibrational energy. An individual example demonstrating the calculated O-atom formation for a gas mixture containing 50% CO in argon at an equilibrium temperature of 5500 K is shown in Fig. 7. The dotted line indicates the time-dependent O atom formation for thermal equilibrium conditions ( $T = T_{\text{trans}} = T_{\text{vib}}$ ). It results in a straight line as proposed earlier. The two solid lines of Fig. 7 were calculated based on the two-temperature model described earlier. The upper curve with  $T = T_{\text{trans}}$  is the result of a computer simulation, in which the dissociation rate coefficient  $k_v$  was deter-

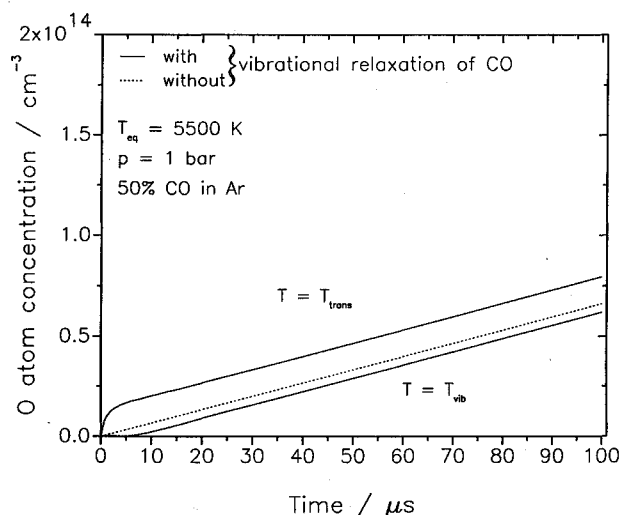


Fig. 7 Computer simulations of the coupling between vibrational relaxation and thermal decomposition of CO: two-temperature model.

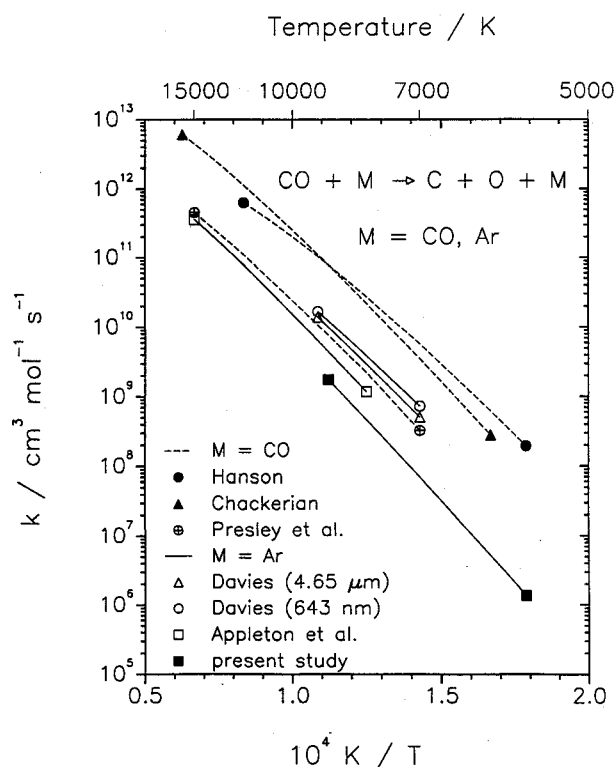


Fig. 8 Comparison between the present results and previous works.

mined based on the translational temperature. It shows in the first 5  $\mu\text{s}$  an accelerated CO formation due to the high post-shock translational temperature, which rapidly decreases to thermal equilibrium. The lower curve in Fig. 7 was calculated assuming the kinetic temperature  $T$  in Eq. (7) equal to  $T = T_{\text{vib}}$ . It results in a delayed formation of O atoms during thermal decomposition of CO, which is again limited to a time period of about 5  $\mu\text{s}$ . This time is significantly shorter than the reaction induction time observed in the present experiments. It shows the inability of the two-temperature model and the rate coefficients used to describe the observed reaction induction period. At longer reaction times  $t \geq 20 \mu\text{s}$  the slopes of all three O-atom concentration curves are nearly identical. This means, translated to our situation, that it is justified to determine rate coefficients according to Eq. (2) from the measured steepest atom concentration slopes under vibrational equilibrium conditions. Note that the CO concentration in the example of Fig. 7 is much higher than in the experiments. The time scale is also different from the experimental results of Fig. 3. All together this indicates that because of the relatively low CO concentrations of our experiments the proposed two-temperature model does not significantly contribute to the interpretation of the experimental results.

A comparison between the present results and rate coefficient data obtained from other studies is illustrated in Fig. 8. The dashed lines summarize the dissociation rate coefficients of CO with  $M = \text{CO}$  as collision partner and the full lines are for  $M = \text{Ar}$  as collision partner. The present data, which are the lowest in the Arrhenius diagram of Fig. 8, agree within the uncertainty limits of the respective experiments with the data of Appleton et al.<sup>1</sup> and Davies.<sup>2</sup> The recommendations of Schofield<sup>9</sup> and Baulch et al.<sup>8</sup> use both these sets of data as reference values and assume error limits of  $\pm 75\%$ . The results of Presley et al.<sup>5</sup> obtained for CO as collision partner are compared to the present results also in the uncertainty limits of the experiments, if the collision efficiency of Ar is assumed to be a factor of 2 lower than that of CO. The rate expression, published by Hanson<sup>3</sup> and Chackerian<sup>4</sup> obtained from experiments in pure CO are not in agreement with the present results.

## V. Conclusion

The resonance absorption spectroscopy was shown to be a sensitive method for studying the high-temperature dissociation of CO by measuring the atomic reaction products O and C. The measured dissociation rate coefficient lies within the uncertainty limits of the data given by Appleton et al.<sup>1</sup> and Davies.<sup>2</sup> The influence of vibrational relaxation on the dissociation process calculated on the basis of a two-temperature model seems to be insignificant under the present reaction conditions and cannot explain observed reaction induction times.

## Acknowledgment

The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

## References

- <sup>1</sup>Appleton, J. P., Steinberg, M., and Liquornik, D. J., "Shock-Tube Study of Carbon Monoxide Dissociation Using Vacuum Ultraviolet Absorption," *Journal of Chemical Physics*, Vol. 52, March 1970, pp. 2205-2221.
- <sup>2</sup>Davies, W. O., "Radiative Energy Transfer on Entry into Mars and Venus," NASA CR-58574, Aug. 1964.
- <sup>3</sup>Hanson, R. K., "Shock-Tube Study of Carbon Monoxide Dissociation Kinetics," *Journal of Chemical Physics*, Vol. 60, June 1974, pp. 4910-4916.
- <sup>4</sup>Chackerian, C., Jr., "The Dissociation of Shock Heated Carbon Monoxide Studied by Two Wavelength Infrared Emission," *Proceedings of the Eighth International Shock Tube Symposium*, Chapman and Hall, London, 1971, pp. 40/1-40/9.
- <sup>5</sup>Presley, L. L., Chackerian, C., Jr., and Watson, R., "Dissociation Rate of Carbon Monoxide between 1000 and 15000 K," AIAA Paper 66-518, 1966.
- <sup>6</sup>Howe, J. T., and Sheaffer, Y. S., "Chemical Relaxation Behind Strong Normal Shock Waves in Carbon Dioxide including Interdependent Dissociation and Ionization Processes," NASA TN D-2131, 1964.
- <sup>7</sup>McKenzie, R. L., "An Estimate of the Chemical Kinetics Behind Normal Shock Waves in Mixtures of Carbon Dioxide and Nitrogen for Conditions Typical of Mars Entry," NASA TN D-3287, Feb. 1966.
- <sup>8</sup>Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., *Evaluated Kinetic Data for High Temperature Reactions*, 1st ed., Vol. 3, Butterworth, London, 1976, pp. 177-186.
- <sup>9</sup>Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," *Journal of Physical and Chemical Reference Data*, Vol. 2, No. 1, 1973, pp. 25-32.
- <sup>10</sup>Fairbairn, A. R., "Presence of an Incubation Time in the Dissociation of CO," *Journal of Chemical Physics*, Vol. 48, 1968, pp. 515-516.
- <sup>11</sup>Fairbairn, A. R., "The Dissociation of Carbon Monoxide," *Proceedings of the Royal Society, A*, Vol. 312, 1969, pp. 207-227.
- <sup>12</sup>Roth, P., "ARAS Messungen an einigen Hochtemperatur-Kohlenwasserstoff-Reaktionen," *Forschung im Ingenieurwesen*, Vol. 46, No. 3, 1980, pp. 93-102.
- <sup>13</sup>Roth, P., and Just, T., "Atomabsorptionsmessungen zur Kinetik der Reaktion  $\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$  im Temperaturbereich 1500 K  $\leq T \leq 2250$  K," *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, Vol. 81, No. 6, 1977, pp. 572-577.
- <sup>14</sup>Thielen, K., and Roth, P., "N Atom Measurements in High-Temperature N<sub>2</sub> Dissociation Kinetics," *AIAA Journal*, Vol. 24, No. 7, 1986, pp. 1102-1105.
- <sup>15</sup>Thielen, K., and Roth, P., "Stoßwellenuntersuchungen zum Start der Reaktion  $\text{CO} + \text{O}_2$ ," *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, Vol. 87, 1983, pp. 920-925.
- <sup>16</sup>Mozzhukin, E., Burmeister, M., and Roth, P., "High Temperature Dissociation of CN," *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, Vol. 93, 1989, pp. 70-75.
- <sup>17</sup>Lutz, A. E., Kee, R. J., and Miller, J. A., "SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis," Sandia National Lab., Rept. SAND87-8248, Albuquerque, NM, Feb. 1988.
- <sup>18</sup>Hooker, W. J., and Millikan, R. C., "Shock-tube Study of Vibrational Relaxation in Carbon Monoxide for the Fundamental and First Overtone," *Journal of Chemical Physics*, Vol. 38, Jan. 1963, pp. 214-220.
- <sup>19</sup>Boyd, R. K., and Burns, G., "Transient Phenomena in Dissociation of Diatomic Molecules," *Canadian Journal of Chemistry*, Vol. 49, 1971, pp. 3744-3754.
- <sup>20</sup>Heims, S. P., "Moment Equations for Vibrational Relaxation Coupled with Dissociation," *Journal of Chemical Physics*, Vol. 38, Feb. 1963, pp. 603-606.
- <sup>21</sup>Mallard, W. G., Westley, F., Herron, J. T., and Hampson, R. F., "NIST Chemical Kinetics Database—Version 4.0," NIST Standard Reference Data, Gaithersburg, MD, April 1992.