

The Decomposition of CO₂ in Glow Discharge

Sergey Y. Savinov*, Hwaung Lee, Hyung Keun Song and Byung-Ki Na†

Clean Technology Research Center, Korea Institute of Science and Technology,
P.O.Box 131 Cheongryang, Seoul 130-650, Korea

(Received 16 February 2002 • accepted 23 March 2002)

Abstract—The energy of the first vibrational level of the N₂ molecule is quite close to the energy of the first level of the asymmetric mode of CO₂. Hence, fast resonance transfer of vibrational energy from N₂ molecules to CO₂, directly populating the necessary level, becomes feasible. As a result of CO₂-CO₂ collision, the population increase of higher vibrational levels of asymmetric mode of CO₂ takes place up to the decomposition of molecules.

Key words: Plasma, Isotopic CO₂, Glow Discharge, Vibrational Excitation

It has been known that the vibrational excitation of molecules essentially accelerates endothermic chemical reaction [Cho et al., 1998; Jeong et al., 2001; Rusanov and Fridman, 1984]. However, it is not always possible to excite the required vibrational mode of molecules selectively by an electric discharge. In our previous work [Savinov et al., 1999; Lee et al., 2001], the decomposition of pure methane and carbon dioxide in a radio-frequency discharge was investigated. It was shown that the dissociation of these molecules was due to the excitation of electronic states. The plasmachemical reactions in nitrogen mixtures were examined in order to analyze the effect of vibrational excitation on reactions involving methane and carbon dioxide.

The plasmachemical reactions involving CO₂ molecules in radio-frequency discharge ($\nu=13.56$ MHz) were investigated by a mass spectroscopic method. A special type of a capacitive discharge was used. A similar discharge system was applied at first for the design of CO₂ gas lasers by N. A. Yatsenko [Raizer et al., 1995] and was lately used in this experiment for plasmachemical purposes [Savinov et al., 1999].

The plasmachemical reactor and the experimental equipment were described in detail in our previous work [Savinov et al., 1999]. The main peculiarity of these reactors was the small size of the electrode sheaths. As a result, almost all the volume of the discharge tube was filled with positive column plasma. The processes were studied under medium pressures. The pressure of gas mixture was changed from 5 to 60 torr.

The radio-frequency generator with a matching network delivered an output power from 0 to 300 W. While measuring discharge input power, we ignored the energy loss through radiation and furthermore suggested that all input powers were absorbed by positive column plasma.

Quadrupole mass spectrometer (Balzers, QMS 200) with Quadstar 421 software was used for qualitative and quantitative analysis of the gas mixtures. The mass spectrometer was connected to the post discharge zone. Some expressions in our previous work [Savinov et al., 1999] were used to define the conversions of initial reactants and molecular flows of reactants and products under investigation. The residence time was considered for the change of the flow-rate by chemical reactions.

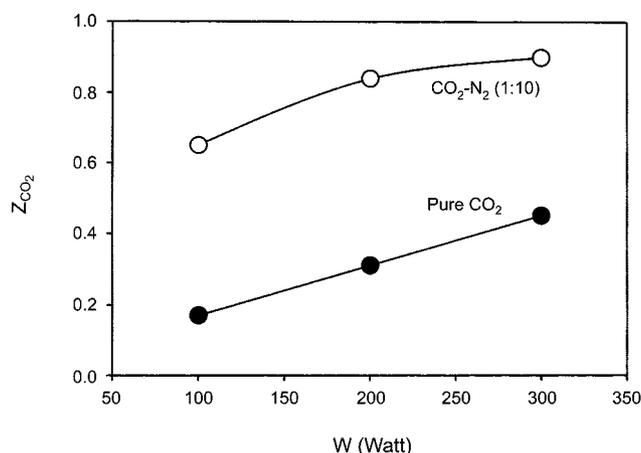


Fig. 1. The dependencies of the conversion of CO₂ on the input power for discharges in the pure CO₂ and the mixture of CO₂ : N₂=1 : 10. Initial conditions: the gas pressure, 21 torr; the flowrate, 55 cm³/min.

nov et al., 1999] were used to define the conversions of initial reactants and molecular flows of reactants and products under investigation. The residence time was considered for the change of the flow-rate by chemical reactions.

The dissociation of CO₂ molecules in the plasma discharge was considered in the mixture with molecular nitrogen. The dependence of conversion of CO₂ molecules on input power is presented in Fig. 1 for the mixture of CO₂ : N₂=1 : 10. The initial pressure of gas mixture was 21 torr, and the flow rate under normal condition was 55 cm³/min. For comparison, this was the same discharge condition in pure CO₂. The conversion of CO₂ in mixture with N₂ was much higher than that in pure CO₂. It was important that the residence times for these cases were almost the same. The rate of CO₂ decomposition in the mixture with nitrogen was faster than that in pure CO₂.

The analysis of mass spectra of gas mixtures in the post plasma zone showed that the only products of CO₂ decomposition in discharge in mixtures with nitrogen were CO and O₂ and the amount of CO was twice as much as that of O₂. It means that the decom-

†To whom correspondence should be addressed.

E-mail: nabk@kist.re.kr

*Present address: P. N. Lebedev Institute, Moscow, Russia

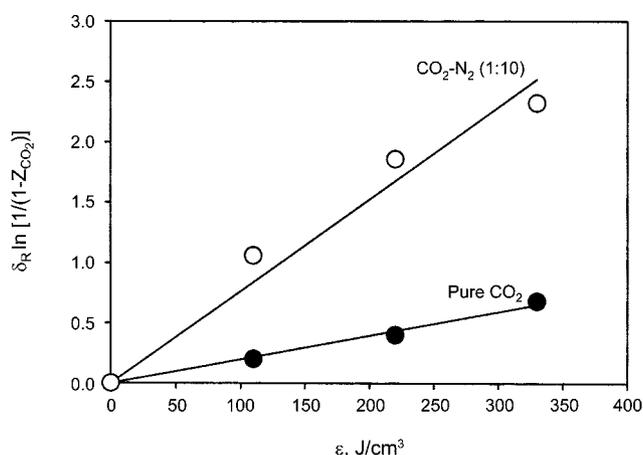


Fig. 2. The dependencies of $\delta_R \ln\{1/(1-Z_{CO_2})\}$ on the specific energy ϵ for discharges in the pure CO₂ and the mixture CO₂-N₂ (1 : 10). Initial conditions: gas pressure, 21 torr; flowrate, 55 cm³/min.

position of CO₂ is due to the process



and the molecular nitrogen is not involved directly in this reaction.

Fig. 2 shows the dependence of $\delta_R \ln\{1/(1-Z_{CO_2})\}$ on specific energy ϵ . Here Z_{CO_2} is the conversion of CO₂, and δ_R is a factor for calibrating the flowrate change due to the chemical reactions. The expressions for Z_{CO_2} and δ_R were obtained from our previous work [Savinov et al., 1999]. It is clear that the dependence is linear and passes the origin of the coordinates if the dissociation of molecules in discharge is caused by the direct electron impact. However, in case of mixture with nitrogen under investigation, the experimental data are not placed within the limits of experimental error to build up the linear dependence traveling through the origin of the coordinates. The dependence of discharge in pure CO₂ is presented in Fig. 2 for a comparison. This clearly demonstrates that the decomposition of CO₂ molecules in discharge in the mixture with nitrogen is not caused by direct electron impact only.

From our viewpoint, in these conditions the dissociation of carbon dioxide molecules is due to the vv-transfer of energy (transfer of vibrational energy between molecules) within the asymmetric mode of CO₂ vibration. The mixture of nitrogen and CO₂ gives the possibility of exciting selectively the asymmetric mode of CO₂ vibration. The energy of the first vibrational level of the N₂ molecule, which is efficiently excited by electron impact in the glow discharge and then slowly relaxes, is quite close to the energy of the first level of the asymmetric mode of CO₂.

The energy difference between them is very small (about 30 K as a temperature scale). This difference is less than the value of room temperature by a factor of 10. Hence, fast resonance transfer of vibrational energy from N₂ molecules to CO₂, directly populating the necessary level becomes feasible. The population of higher vibrational levels of asymmetric mode of CO₂ increases as a result of CO₂-CO₂ collisions. This is similar to the microwave discharge in pure CO₂ under medium pressures [Rusanov and Fridman, 1984].

It was shown earlier that the plasmachemical reactions stimu-

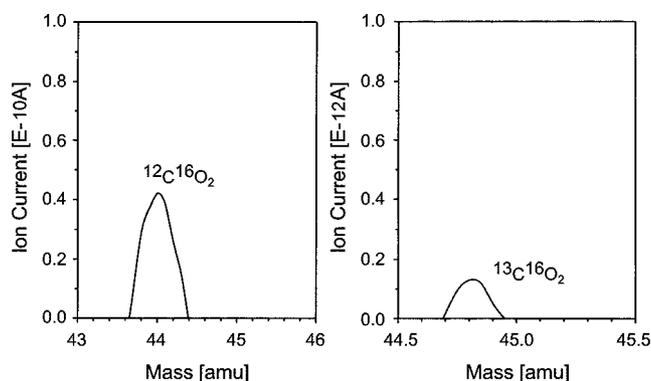


Fig. 3. The intensity of isotopic CO₂ mass spectrum without discharge.

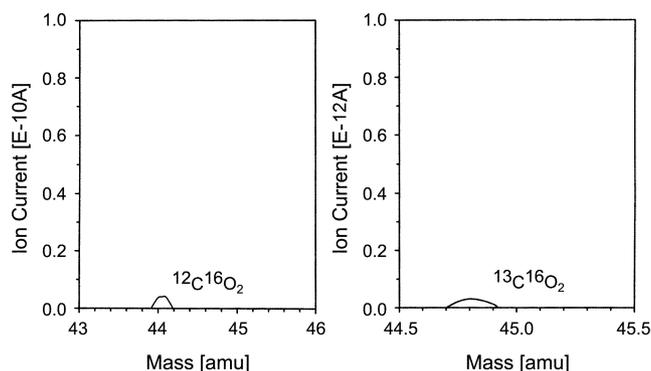


Fig. 4. The intensity of isotopic CO₂ mass spectrum in the post plasma zone. Initial conditions: the mixture of CO₂ : N₂ = 1 : 3; the total pressure, 60 Torr; the total flowrate, 100 cm³/min; the input power, 300 Watts.

lated by vibrational excitation of molecules must demonstrate the reverse isotope effect [Andreev et al., 1994; Slovetshii, 1980]. The reaction rate of light isotopes must be higher than that of heavy isotopes.

Natural carbon dioxide is a mixture of stable isotopes. The heavy isotope of ¹³C¹⁶O₂ is approximately 1.1% of the light isotope of ¹²C¹⁶O₂. The conversion of these components was measured in rf-discharge in mixture with nitrogen. Figs. 3 and 4 show fragments of mass spectrum of CO₂.

The peak at m=44 belongs to ¹²C¹⁶O₂ and the peak at m=45 belongs to ¹³C¹⁶O₂. The amplification for the left-hand sides of these figures was less than that for the right-hand sides by a factor of 100. Each of these spectra was obtained in the framework of the same experiment. At the initial conditions, the pressure was 60 torr and total flow rate was $V^{(10)}=100$ cm³/min with CO₂ : N₂ = 1 : 3.

The mass spectrum of Fig. 3 was obtained without discharge, and the mass spectrum of Fig. 4 was obtained with rf-discharge at the input power of 300 W. From these spectra it was possible to estimate the degree of dissociation for ¹²C¹⁶O₂ and ¹³C¹⁶O₂. The dissociation of ¹²C¹⁶O₂ was about 96%, and that of ¹³C¹⁶O₂ was about 70%. The dissociation rate of ¹²C¹⁶O₂ was higher than that of ¹³C¹⁶O₂. The reverse isotope effect in this observation gave evidence that the decomposition of the CO₂ molecules was caused by vv-transfer of energy within the asymmetric mode of CO₂ vibration.

An experimental study of plasmachemical reaction involving CO₂ molecules with N₂ in rf discharge was investigated with a mass spectroscopic method. The reaction products of CO₂ decomposition were CO and O₂. When CO₂ dissociation reaction with N₂ occurred, the dissociation of CO₂ molecules was due to the vv-transfer of energy within the asymmetric mode of CO₂ vibration. The energy of the first vibrational level of the N₂ molecule was quite close to the energy of the first level of the asymmetric mode of CO₂. Hence, fast resonance transfer of vibrational energy from N₂ molecules to CO₂, directly populating the necessary level became feasible. Thereafter, as the result of CO₂-CO₂ collisions, the population of higher vibrational levels of asymmetric mode of CO₂ increased and the decomposition of molecules took place.

REFERENCES

- Andreev, S. N., Kerimkulov, M. A., Marurenko, A. A., Ochkin, V. N., Savinov, S. Y. and Jikhai, S. N., "Isotope Effects in the Dissociation of Carbon Dioxide in Nonequilibrium Gas Discharge Plasma," *Tech. Phys. V.*, **39**(5), 466 (1994).
- Cho, W., Baek, Y., Pang, H. and Kim, Y. C., "A Direct Catalytic Conversion of Natural Gas to C₂+Hydrocarbons by Microwave Plasma," *Korean J. Chem. Eng.*, **15**, 500 (1998).
- Jeong, H. K., Kim, S. C., Han, C., Lee, H., Song, H. K. and Na, B. K., "Conversion of Methane to Higher Hydrocarbons in Pulsed DC Barrier Discharge at Atmospheric Pressure," *Korean J. Chem. Eng.*, **18**, 196 (2001).
- Lee, H., Savinov, Y. S., Song, H. K. and Na, B. K., "Estimation of the Methane Conversion in a Capacitively Coupled Radio-Frequency Discharge," *J. Chem. Eng. Jpn.*, **34**(11), 1356 (2001).
- Raizer, Y. P., Shneider, U. N. and Yatsenko, N. A., "Radio-Frequency Capacitive Discharges," CRC Press, N.Y. (1995).
- Rusanov, V. D. and Fridman, A. A., "Physics of Chemically Active Plasma," Moscow, Nauka (1984).
- Savinov, Y. S., Lee, H., Song, H. K. and Na, B. K., "Decomposition of Methane and Carbon Dioxide in a Radio-Frequency Discharge," *Ind. Eng. Chem. Res.*, **38**(7), 2540 (1999).
- Slovetskhii, D. I., "Mechanism of Chemical Reactions in Nonequilibrium Plasma," Moscow, Nauka (1980).