4. Isotope Separation in Discharge Plasmas of Molecular Gases

EZOUBTCHENKO, Alexandre N., AKATSUKA Hiroshi and SUZUKI Masaaki
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo 152-8550, Japan
(Received 25 December 1997)

Abstract
We review the theoretical principles and the experimental methods of isotope separation achieved through the use of discharge plasmas of molecular gases. Isotope separation has been accomplished in various plasma chemical reactions. It is experimentally and theoretically shown that a state of non-equilibrium in the plasmas, especially in the vibrational distribution functions, is essential for the isotope redistribution in the reagents and products. Examples of the reactions, together with the isotope separation factors known up to the present time, are shown to separate isotopic species of carbon, nitrogen and oxygen molecules in the plasma phase, generated by glow discharge and microwave discharge.

Keywords:
isotope separation, vibrational nonequilibrium, glow discharge, microwave discharge, plasma chemistry

4.1 Introduction
Plasmas generated by electric discharge of molecular gases under moderate pressures (10 Torr < p < 200 Torr) are usually in a state of nonequilibrium. We can define various temperatures according to the kinetics of various particles in such plasmas, for example, electron temperature (T_e), gas translational temperature (T_0), gas rotational temperature (T_R) and vibrational temperature (T_v), where the relationships T_e > T_v ~ T_R ~ T_0 usually hold. Especially pronounced nonequilibrium is found in the plasmas of N_2, CO_2 and CO discharges. The high vibrational temperature can activate some endothermic reactions of the molecules listed above, and at the same time, lower T_0 prevents reversal exothermic reactions, which can not be activated by vibrations. Since isotopic species of these gases have different vibrational quanta, they can have different vibrational distribution functions (VDF). This phenomenon is similar to the Treanor effect in the VDF of anharmonic oscillators [1]. It can result in the different rate constants of endothermic reactions, therefore the isotopic species will be redistributed between the reagents and the products. We can elaborate a new method of the plasma isotope separation for light elements.

There were a few experimental studies of isotope separation phenomena in the nonequilibrium electric discharge. Semiokhin et al. measured CO_2 enrichment in ^13CO_2 and ^12C^16O^18O with a separation factor α = 1.01 in the CO_2 silent (barrier) discharge in the pressure range of 100 - 760 Torr [2]. They measured O_2 enrichment in ^16O with α = 1.09 through dissociation of CO_2, and nondissociated CO_2 enrichment in ^13C with α = 1.024 in the glow discharge plasma of pure CO_2 (30 - 100 Torr). They also observed relatively high (α ≈ 1.10) ozone enrichment in ^16O during ozone synthesis in the O_2 silent discharge under 760 Torr [3]. The latter seems to be profitable for oxygen isotope enrichment because of relatively small energy cost of ozone molecule (~ 15 - 20 eV) in the industrial ozonizers. There were, however, no further investigations in this field. The silent discharge in the molecular
gases provides a nonequilibrium condition \((T_e \gg T_0)\), but the role of vibrations was not elucidated.

The important role of vibrations in the gas discharge became clear when the CO and CO\(_2\) plasmas were discovered to be active media for infrared lasers. It was established both theoretically and experimentally that CO, CO\(_2\), and N\(_2\) can be easily vibrationally excited by an electron impact in the glow discharge with a high rate constant \(k_{vv} \approx 10^{-8} \text{ cm}^3/\text{s}\) at \(T_e \approx 1 - 2 \text{ eV}\). A resonance exchange of vibrational quanta between the same molecular species usually has the rate constant \(k_{vv} \approx 10^{-11} - 10^{-9} \text{ cm}^3/\text{s}\), which is much larger than that of vibration-to-translation energy transfer \(k_{vt} \approx 10^{-19} - 10^{-14} \text{ cm}^3/\text{s}\). It is the fundamentals for the vibrationally nonequilibrium state in the gas discharge with an appropriate pressure and an ionization degree.

4.2 Basic qualitative concepts of possible separation phenomena in the vibrationally nonequilibrium gas discharge plasmas

In discharging plasmas of diatomic or triatomic gaseous molecules, it is well-known that it is possible to direct most of the electron energy into the molecular vibrational energy, by adjusting the reduced electric field \(E/N\) into the range of \((2 - 6) \times 10^{-16} \text{ V} \cdot \text{cm}^2\) \([4]\). For example, the energy balance of the electrons in the CO\(_2\) plasma is shown in Fig. 1 as a function of \(E/N\), which controls \(T_e\). A rate constant of the excitation of the lower lying vibrational levels of CO\(_2\) by an electron impact is estimated to be \(k_{vv} \approx 10^{-8} \text{ cm}^3/\text{s}\) at \(T_e = 1 \text{ eV}\). We can estimate \(k_{vv}\) to be \(10^{-9} \text{ cm}^3/\text{s}\) at \(T_0 = 300 \text{ K}\) for lower lying vibrational levels of CO\(_2\) and \(k_{vt} \approx 10^{-12} \text{ cm}^3/\text{s}\) for the fastest process of CO\(_2\) \(v_l\) bending mode. Therefore some kinds of a vibrational population distribution will be formed with \(T_{10} = (h\nu/(kln(N_0/ N_1))) \gg T_0\), where \(h\) is the Planck constant, \(k\) is the Boltzmann constant, \(N_1\) and \(N_0\) are the number densities of the population of the first excited vibrational level and of the ground state, respectively. For a diatomic gas CO, such a VDF was experimentally measured up to the 40th vibrationally excited level. As an example, the VDF’s for the components of \(^{12}\text{C}^{16}\text{O}, ^{13}\text{C}^{16}\text{O}\) and \(^{12}\text{C}^{18}\text{O}\) are shown in Fig. 2 \([5]\). We can see that they are not Boltzmann distributions, but that each of them has a plateau for \((5 - 7) < \nu < (30 - 40)\), where \(\nu\) is the vibrational quantum number. Such characteristics of the VDF are determined by the anharmonicity of molecular vibrations. The drop with the angle \(\sim 1/T_0\) in the populations of the highly excited levels appears when \(k_{vt}\), which is proportional to \(\nu\), becomes larger than \(k_{vv}\).

We have to consider more complicated systems of the vibrational excitations in triatomic gaseous molecules, since they have plural vibrational modes. Bailly et al. measured a VDF for the CO\(_2\) \(v_3\) asymmetric mode in the glow discharge of the mixture of CO\(_2\) - N\(_2\) - He for a CO\(_2\) laser up to \(v_3 \leq 10\) \([6]\). They showed that an observed VDF slightly deviated from the Boltzmann
distribution in the region of $v_3 = 7 - 8$.

Belenov et al. first suggested the possibility of application of the vibrational nonequilibrium for isotope separation [7]. Subsequently, the difference in a VDF for isotopic species of diatomic gaseous molecules, such as $^{12}$C$^{16}$O - $^{13}$C$^{16}$O or $^{14}$N$^{14}$N - $^{15}$N$^{14}$N, was calculated [8, 9]. It is shown that there will be a strong difference in the population of highly excited vibrational levels for isotopic components when we keep $T_{10} \gg T_p$. Figure 3 shows the strong excess of the populations of the vibrationally excited states for $^{13}$C$^{16}$O and $^{12}$C$^{18}$O in the CO - N$_2$ - He glow discharge. The ratio amounts to about 5 times as much as that of their natural abundance [5]. Such excess will give a difference in the rate constants for some endothermic reactions activated by vibrational energy of isotopic components.

The reaction rate itself even changes the sign of isotope enrichment [10]. Let us consider that gaseous diatomic molecules consist of two isotopic variations A and B, where $m_A > m_B$ for their masses and $N_{0A} \ll N_{0B}$ for their densities. Here, the VDF of the molecule B will be formed by collisions of molecules B and B, and the vibrational energy of each molecule will be transferred with each other by resonance energy transfer (this type of collisions is called a V - V exchange). On the other hand, the VDF of the molecule A will be formed mainly by collisions of A - B, where the vibrational energy levels of both molecules do not coincide each other. In this case, the vibrational energy will be transferred through a quasiresonance energy exchange, which is called a V - V' quasiresonance exchange, similar to the exchange among anharmonic oscillators, but with a larger resonance defect. A qualitative diagram of a possible VDF for the not rapid chemical reaction is shown in Fig. 4, where $E_a$ and $E'_a$ are the possible activation energy of the reaction. The activation energy $E_a$ in Fig. 4 makes the reaction products enriched in the A component. Meanwhile, the activation energy $E'_a$ results in the opposite sign.

Concerning a rapid chemical reaction with the rate constant $k_R$, that is, when the drop of the VDF is
determined not by $k_{VT}$ but by $k_R$, the qualitative scheme for the VDF is shown in Fig. 5. At this time the component B will react faster than the component A.

### 4.3 Experiments on vibrationally nonequilibrium plasmas

Basov et al. found the isotope separation in a vibrationally nonequilibrium plasma for the first time in the world [11]. They measured the enrichment in $^{15}$N of nitrogen oxide after the impulse glow discharge in the mixture of $N_2$ - $O_2$ cooled by LN$_2$ through the process

$$N_2 + O_2 = 2NO.$$  \hspace{1cm} (1)

The main elementary processes were considered to be the followings:

$$O_2 + e^- = 2O + e^-,$$  \hspace{1cm} (2)

$$O + N_2(v) = NO + N$$

with the activation energy $E_a = 3.3$ eV, \hspace{1cm} (3)

$$N + O_2(v) = NO + O$$

with $E_a = 0.3$ eV. \hspace{1cm} (4)

Equation (3) seemed to be isotopically selective due to a different population of the appropriate levels near $E_a$, namely at $v = 12$, for $^{14}$N$^{14}$N and $^{15}$N$^{14}$N components, where $^{15}$N$^{14}$N was considered to have larger populations. Equation (4) was not considered to be isotopically selective with respect to oxygen isotopes, because of the small influence of vibrations on the reaction due to the small activation energy.

Further investigations of Eq. (1) did not confirm large separation factors. The separation factors up to $\alpha = 1.2$ were observed [12, 13]. They were smaller than the theoretically possible ones for a pure vibrational excitation in Eq. (1). It can be explained by the existence of nonselective channels of NO production in the $N_2$ - $O_2$ glow discharge, such as the production of nitrogen atoms by an electron impact with a subsequent nonselective stage (4) of NO production.

Another possible candidate for carbon and oxygen isotope enrichment was the reaction of CO disproportionation

$$CO(v) + CO(v) = C + CO_2$$

with $E_a = 6$ eV. \hspace{1cm} (5)

In a LN$_2$ cooled CO impulse glow discharge, Abzianidze et al. observed small CO enrichment in $^{13}$C and $\alpha = 5$ in the ion C$_2$O$^+$, which was supposedly produced under a fragmental ionization in the mass-spectrometer from carbon suboxide C$_2$O$_2$ [14]. The possible selectivity of Eq. (5) is determined by the strong difference in VDF’s of $^{12}$C$^{16}$O, $^{13}$C$^{16}$O and $^{12}$C$^{18}$O (see Fig. 3). The isotopic effect in Eq. (5) in the glow discharge can be masked by another channel of CO decomposition (by a direct electron impact, which seems to be nonselective), and by subsequent nonselective reactions of atomic carbon. Gorse et al. showed the conditions of the glow discharge for the predominance of pure vibrational CO dissociation mechanisms [15].

With respect to the possible isotope separation in a nonequilibrium plasma, a group of P.N. Lebedev Institute studied the reaction of the carbon dioxide decomposition in the glow and microwave discharges [10, 16].

$$CO_2 = CO + 1/2 O_2.$$  \hspace{1cm} (6)

The concept of their study was the same as in the previous investigation of Eqs. (3) and (5). Isotopically variant molecules $^{13}$CO$_2$ and $^{12}$CO$_2$ can have different populations in highly excited vibrational levels, therefore their rates of dissociation into CO molecules are different from each other. There can be two possible channels of dissociation: (1) through the excitation of vibrational levels up to the dissociation energy

$$CO_2(v) \rightarrow CO + O$$

with $E_a = 5.5$ eV, \hspace{1cm} (7)

or (2) the direct excitation by an electron impact

$$CO_2 + e^- \rightarrow CO_2^* \rightarrow CO + O + e^-.$$  \hspace{1cm} (8)

It depends on the discharge conditions which channel is dominant. The most probable final stage of CO$_2$ decomposition is as follows:

$$CO_2(v) + O = CO + O_2$$

with $E_a = 1.5$ eV. \hspace{1cm} (9)

This reaction seems to be isotopically nonselective or can have an opposite effect to Eq. (7) concerning the sign of selectivity.

By spectroscopic measurements of the ratio $^{13}$CO/ $^{12}$CO in the gas mixture of CO$_2$, CO and O$_2$ after a glow discharge in the initially pure CO$_2$, it was shown that CO was enriched in $^{13}$C with $\alpha \approx 1.3$, whereas carbon monoxide produced after a glow discharge in the CO$_2$ laser mixture CO$_2$ - $N_2$ - He was depleted in $^{13}$C with $\alpha \approx 2$ [10]. They explained the results by assuming the different CO$_2$ dissociation channels. In the pure CO$_2$ discharge, the electron temperature was $T_e = 2 - 3$ eV. CO$_2$ dissociates mostly by a direct electron impact from the lower lying CO$_2$ vibrational levels. Under this condition, $^{12}$CO$_2$ dissociates faster (see Fig. 4). On the other hand, in the mixture CO$_2$ - $N_2$ - He, the electron temperature $T_e \leq 1$ eV, which is the best conditions for CO$_2$ vibrational excitation (see Fig. 1). Consequently, these conditions establish the relation-
ship \( k_0 \gg k_v \), therefore \(^{12}\text{CO}_2\) dissociates faster (see Fig. 5). The carbon monoxide produced by microwave discharge in pure \(^{12}\text{CO}_2\) under moderate pressure (\( \approx 100 \) Torr) was also depleted in \(^{13}\text{C}\) with \( \alpha = 2.5 \), where \( T_v \approx 1 \) eV and the dissociation is mainly attributed to the vibrational one. The dissociation degree of \(^{12}\text{CO}_2\) was about 25 \%, which meant that the nondisassociated \(^{12}\text{CO}_2\) was enriched in \(^{13}\text{C}\) with \( \alpha \approx 1.3 \).

As an example, an experimental scheme for the \(^{12}\text{CO}_2\) dissociation in a microwave discharge is shown in Fig. 6 [17]. The microwave generator was operated at the frequency 2.45 GHz (\( \lambda_0 = 12.2 \) cm). Its output power was up to 5 kW. The microwave was fed through rectangular waveguides with its dimension of 110 \times 55 mm\(^2\), 90 \times 45 mm\(^2\) and 72 \times 34 mm\(^2\), which were terminated by a closed-end short circuit or by a water cooled load. The plasma chemical reactor was made of a quartz tube of its inner diameter 26 – 28 mm, crossing the waveguide perpendicularly to the wide side. The \(^{12}\text{CO}_2\) flow was regulated by a flow-meter within the range of 0.1 – 0.6 nl/s. The power absorbed by the plasma was 1 – 2 kW, and the discharging pressure was about 100 Torr, which meant \( E/N = (2 - 5) \times 10^{-16} \) Vcm\(^2\). The gas temperature measured in the after-discharge flow was relatively small (\( \approx 700 \) K), whereas the vibrational temperature in the discharging region was about 3,000 K. The difference in these two temperatures explains the observed isotopic effects.

When we take account of the small specific energy consumed in the microwave discharge (\( E_w = 1 - 5 \) eV/molecule \(^{12}\text{CO}_2\)) and a large throughput of the device (0.5 g \(^{12}\text{CO}_2\)/s), it is evident that the further study of this phenomenon gives us a profitable method of carbon and oxygen isotope enrichment.

The possibility of isotope separation by Eqs. (3) and (5) was also demonstrated in the nonequilibrium conditions created by another method being different from electron impact. For example, Akulintsev et al. studied the carbon isotope separation in the expanding hot gaseous mixture of CO and Ar passing through a Laval nozzle, where the relationship \( T_v \gg T_0 \) also holds [18]. They reported that separation factors of the carbon isotopes were \( \alpha = 2 - 6 \).

In addition, Eq. (5) was investigated in a CO gas pumped optically by a CO laser [19]. Spectroscopic measurements of a C\(_2\) visible emission from the gas volume revealed that the diatomic carbon molecule was enriched in \(^{13}\text{C}^{12}\text{C}\), whose molar fraction became up to 8 \% of that of \(^{12}\text{C}^{12}\text{C}\). It means that the significant selectivity was accomplished mainly through Eq. (5). The subsequent reactions of carbon with CO, however, made the carbon into a stable compound \(^{12}\text{C}^{12}\text{O}_2\) polymer, where the final separation factor was only \( \alpha = 1.2 \).

When we study the carbon isotope separation under the conditions of a large (\( > 25 \) \%) \(^{12}\text{CO}_2\) dissociation degree, we have to take account of possible \(^{12}\text{CO}_2\) - CO exchange reactions, such as exchange by an oxygen atom,

\[ ^{12}\text{CO}_2 + ^{13}\text{CO} \leftrightarrow ^{12}\text{CO} + ^{13}\text{CO}_2 \]  

We can see that this reaction leads to the carbon isotope redistribution between \(^{12}\text{CO}_2\) and CO. An equilibrium constant for Eq. (10) at \( T = 300 \) K was calculated to be 1.055 by Urey [20], shifted to the right. Of course, rate constants for forward and reversal reactions are small at room temperature. Under conditions of microwave discharge, however, the rate constant of this exchange reaction may be as large as that of the \(^{12}\text{CO}_2\) dissociation. It is not clear whether the equilibrium constant of Eq. (10) is larger than 1 or not, because both reactions are activated by \(^{12}\text{CO}_2\) and CO vibrations.

Exchange reactions

\[ ^{16}\text{O}^{16}\text{O} + ^{18}\text{O}^{16}\text{O} \leftrightarrow ^{16}\text{O}^{18}\text{O} + ^{18}\text{O}^{16}\text{O} \]  

can lead to \(^{12}\text{CO}_2\) enrichment in \(^{18}\text{O}\). This reaction was studied in a plasma generated by a silent discharge [2]. They measured \(^{12}\text{CO}_2\) enrichment in \(^{18}\text{O}\) with \( \alpha = 1.024 \), whereas the equilibrium constant for Eq. (11) at \( T = 600 \) K was calculated to be 1.011.

Jaffe and Klein studied the rate constants of the following exchange reaction [21]
$^{18}\text{O} + \text{C}^{16}\text{O} \leftrightarrow ^{16}\text{O} + \text{C}^{18}\text{O}$.  

(12)

Atomic oxygen is present with the concentration of 1 − 2% in the CO$_2$ dissociation process, which contributes the oxygen isotope redistribution through Eq. (12).

### 4.4 Conclusions

It was theoretically described that the vibrational nonequilibrium in the molecular gases having isotopic components should give perceptible isotopic effects in plasma chemical reactions. Experiments on vibrationally nonequilibrium plasmas have shown isotope separation factors which should be used practically for isotope enrichment of light elements. Further investigations are necessary to find the most favorable gas discharge conditions and chemical reagents in the nonequilibrium plasma chemistry of isotopic mixtures.

### References


