

Observation of an inverse isotope effect in the plasma-chemical decomposition of carbon dioxide

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It has been discovered that an inverse isotope effect has a significant influence on the conversion of CO_2 into CO in a microwave discharge. At an energy deposition $J = 7 \text{ J/cm}^3$ the extent of the conversion of $^{12}\text{C}^{16}\text{O}_2$ is 2.5 times that for the isotope $^{13}\text{C}^{16}\text{O}_2$.

A nonresonant VV' exchange of vibrational quanta between different molecules plays an important role in shaping the vibrational distribution functions of the particles in nonequilibrium molecular systems. Even if the difference between the masses of the molecules is very small, as it is in the case of isotopes, for example, the VV' exchange can lead to substantial differences in the vibrational excitation of the different molecular components. These differences in turn have a significant effect on the overall vibrational kinetics of nonequilibrium systems. Belenov *et al.*¹ were the first to suggest exploiting the particular features of VV' energy exchange in a gas of diatomic molecules to achieve isotope separation. The basic idea is as follows: A Treanor distribution is obtained for each component in a mixture of isotopes. The lower-frequency oscillators (the molecules of the heavy isotope) are excited more efficiently. The situation is illustrated by Fig. 1, which is a sketch of the vibrational distribution functions of the molecules of two isotopes (a heavy isotope 1 and a light one 2). A difference in the degree of vibrational excitation can lead to a "direct" isotope effect for processes which were stimulated by vibrational excitation. It is easy to see that if the activation energy of the process, E_a , corresponds to the plateau region of the distributions, then the rate of this process will be higher for the heavy isotope. After the paper by Belenov *et al.*¹ appeared in 1973, a large number of theoretical and experimental studies were undertaken to learn about and make use of the isotope effect for separating stable isotopes through vibrational exchange. That research was discussed in detail and analyzed critically in a review by Rich and Bergman.²

In 1980, Macheret *et al.*³ first pointed out the possibility of separating the lighter isotope by means of vibrational exchange. That process has come to be known as the "inverse isotope effect." Macheret *et al.*³ discussed a mixture of isotopes in which the component with the higher mass was a small admixture. In this case the vibrational distribution function for the heavy isotope is shaped by VV -exchange processes, whose rate is usually much lower than the rate of VV' exchange, because of the large resonance defect. The VV exchange dominates the shaping of the vibrational distribution for the light isotope. The distribution function for VT relaxation is thus cut off earlier for the heavy isotope. This circumstance is reflected in Fig. 1. Here E_1 and E_2 are the energies at which the distribution functions for the heavy and light isotopes, respecti-

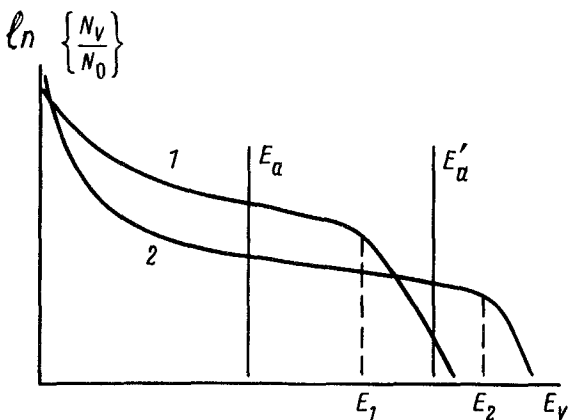


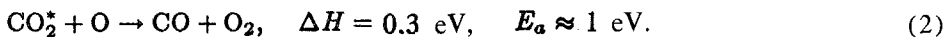
FIG. 1. Vibrational distribution functions of the molecules of two isotopes (1 and 2).

vely, are cut off. If molecules are participating in processes for which the activation barrier E'_a satisfies the condition $E_1 < E'_a < E_2$, we will observe an inverse isotope effect. The rates of reactions involving the lighter isotope will be higher than those for the heavy isotope. The difference in rates may be substantially higher for the inverse isotope effect than for the direct one. To the best of our knowledge, no experimental evidence of the inverse isotope effect has previously been observed.

We have observed a significant influence of the inverse isotope effect in the conversion of CO_2 into CO in a microwave discharge at intermediate pressures. It was assumed⁴ that under these conditions the plasma electrons excite primarily the low-lying vibrational levels of the CO_2 molecules, while the higher levels are populated by VV exchange. Molecules which have a sufficient energy undergo a dissociation:



The atomic oxygen produced in reaction (1) then undergoes a secondary reaction with vibrationally excited CO_2^* molecules:



A leading role is played in these processes by vibrations corresponding to an antisymmetric mode, since it interacts least with the translational degrees of freedom. A large fraction of the energy deposited in the discharge can be put in the antisymmetric CO_2 mode.

The carbon dioxide was decomposed in a plasma-chemical reactor. Microwave radiation from a source with a maximum power $W = 1.8 \text{ kW}$ and a frequency $f = 2.4 \text{ GHz}$ was fed into a rectangular waveguide with a cross section of $90 \times 45 \text{ mm}$. The active zone of the reactor, a quartz tube with an inside diameter of 27 mm , intersects this waveguide along the direction perpendicular to the broad wall of the waveguide. The waveguide terminates in a calorimetric load, which is used to determine the power supplied by the source. The gas flow rate through the reactor was varied by a rotameter over the range $0.1\text{--}0.3 \text{ liter/s}$. The gas pressure at the inlet was $p = 70\text{--}120$

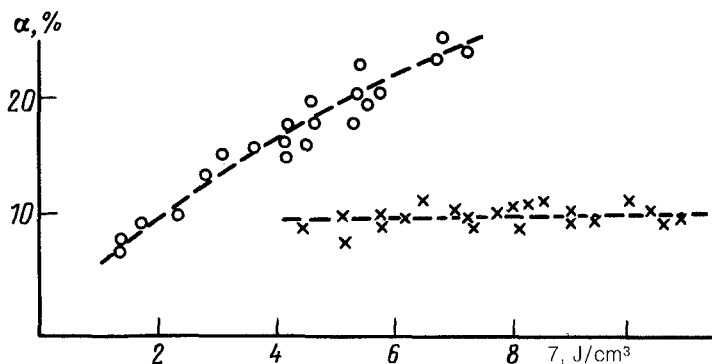


FIG. 2. Extent of CO_2 conversion versus the energy deposition in the discharge. \circ — $^{12}\text{C}^{16}\text{O}_2$; \times — $^{13}\text{C}^{16}\text{O}_2$.

Torr. A special gas distributor imparted a tangential velocity component to the gas flow; the result was to stabilize the discharge at the axis and to provide thermal insulation for the tube wall. At the exit from the reactor the gas was cooled to room temperature and passed through a cell. The extent of conversion of CO_2 into CO was determined by absorption spectroscopy on a laser-diode spectrometer,⁵ on the basis of the absorption at various rotational lines of the 0–1 vibrational transition of the $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ molecules in the cell. The experimental procedure is described in Ref. 5.

Figure 2 shows the extent of the CO_2 conversion versus the energy deposited in the discharge for the isotopes $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$. The magnetron power was held at a constant level, and the gas flow rate was varied. We see that the extent of $^{12}\text{C}^{16}\text{O}_2$ conversion increases monotonically with increasing energy deposition under these particular conditions ($p \sim 100$ Torr), while the extent of $^{13}\text{C}^{16}\text{O}_2$ conversion remains constant ($\alpha \approx 10\%$). At high levels of the energy deposition, this quantity is significantly higher for the isotope $^{12}\text{C}^{16}\text{O}_2$: at $J = 7 \text{ J/cm}^3$, for example, we find $\alpha = 25\%$.

We believe that this behavior of the degree of conversion for the different isotopes is governed by an inverse isotope effect. Specifically, the CO_2 which was used was an isotopic mixture in which the isotope with the larger mass, $^{13}\text{C}^{16}\text{O}_2$, constituted a small admixture ($|^{13}\text{C}^{16}\text{O}_2/^{12}\text{C}^{16}\text{O}_2| \approx 1, 1\%$). The size of the vibrational quantum of the antisymmetric mode for $^{12}\text{C}^{16}\text{O}_2$ is 2349.14 cm^{-1} , while that for $^{13}\text{C}^{16}\text{O}_2$ is smaller by 65.66 cm^{-1} . As the energy deposition is increased, the gas temperature obviously increases, and the efficiency of VV processes correspondingly increases. The VV' -exchange processes, which shape the plateau on the $^{13}\text{C}^{16}\text{O}_2$ vibrational distribution function, cannot bring about an increase in the degree of conversion for this isotope. The vibrational distribution function for the $^{12}\text{C}^{16}\text{O}_2$, on the other hand, is shaped by VV exchange. As a result, the degree of conversion for the $^{12}\text{C}^{16}\text{O}_2$ is significantly higher than that for the isotope $^{13}\text{C}^{16}\text{O}_2$ at high values of the energy deposition.

These results constitute the first clear evidence of an inverse isotope effect. Although the plasma-chemical system used here was not carefully optimized, we were able to achieve a completely noticeable difference in the formation rates of the isotopes $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$. One can therefore hope that plasma-chemical decomposition of

CO₂ in a microwave discharge can ultimately be developed into a method for separating stable isotopes.

¹É. M. Belenov, E. P. Markin, A. N. Oraevskii, and V. I. Romanenko, *Pis'ma Zh. Eksp. Teor. Fiz.* **18**, 196 (1973) [*JETP Lett.* **18**, 116 (1973)].

²J. W. Rich and R. Bergman, in: *Nonequilibrium Vibrational Kinetics* (ed. M. Capitelli), Springer-Verlag, New York, 1986.

³S. O. Macheret, V. D. Rusanov, A. A. Fridman, and G. V. Sholin, *Dokl. Akad. Nauk SSSR* **255**, 98 (1980) [*Sov. Phys. Dokl.* **25**, 925 (1980)].

⁴V. D. Rusanov and A. A. Fridman, *Physics of a Chemically Active Plasma*, Nauka, Moscow, 1984.

⁵A. V. Dem'yanenko, I. I. Zasavitskii, V. N. Ochkin *et al.*, *Kvant. Elektron. (Moscow)* **14**, 851 (1987) [*Sov. J. Quantum Electron.* **17**, 536 (1987)].

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