

# Tunneling Chemical Reactions of Cold Molecules

Takamasa Momose,  
*Division of Chemistry, Graduate School of Science, Kyoto University,  
Kyoto, 606-8502 JAPAN*

The tunneling effect becomes important in chemical reactions at low temperatures because of the suppression of thermally activated reaction processes. Such a situation is expected to be realized in interstellar clouds, for example, where molecules are produced at 5 ~ 50 K. However, direct observation of the tunneling process in chemical reactions in laboratories is not easy because most systems are immobilized by condensation at low temperatures.

Solid parahydrogen is a unique matrix for the study of chemical reactions of cold molecules.[1,2] By virtue of the softness of solid parahydrogen as a quantum crystal, rotational motion of molecules in the crystal are well quantized as in the gas phase. Moreover, molecules are mobile in the crystal, so that various chemical reactions occur in the crystal. As a result, quantitative information on chemical reactions of nearly free molecules at liquid He temperatures can be obtained directly including tunneling effect.

In the present work, tunneling chemical reactions between deuterated methyl radicals and the hydrogen molecule in a parahydrogen crystal have been studied by FTIR spectroscopy. The tunneling rates of the reactions  $R + H_2 \rightarrow RH + H$  ( $R=CD_3$ ,  $CD_2H$ ,  $CHD_2$ , and  $CH_3$ ) in the vibrational ground state were determined directly from the temporal change in the intensity of the rovibrational absorption bands of the reactants and products in each reaction in solid parahydrogen observed at 5 K. The tunneling rate of each reaction was found to differ definitely depending upon the degree of deuteration in the methyl radicals. The tunneling rates were determined to be  $3.3 \times 10^{-6} \text{ s}^{-1}$ ,  $2.0 \times 10^{-6} \text{ s}^{-1}$ , and  $1.0 \times 10^{-6} \text{ s}^{-1}$  for the systems of  $CD_3$ ,  $CD_2H$ , and  $CHD_2$ , respectively. Conversely, the tunneling reaction between a  $CH_3$  radical and the hydrogen molecule did not proceed within a week's time. The upper limit of the tunneling rate of the reaction of the  $CH_3$  radical was estimated to be  $8 \times 10^8 \text{ s}^{-1}$ . The tunneling reaction rates are clearly faster for heavier isotopomers in these systems. The "anomalous" deuteration effect will be discussed.

1. T. Momose, and T. Shida, Bull. Chem. Soc. Jpn, **71**, 1 (1998).
2. T. Momose, H. Hoshina, M. Fushitani, and H. Katsuki, Vib. Spectrosc. **34**, 95 (2004).
3. T. Momose, H. Hoshina, N. Sogoshi, H. Katsuki, T. Wakabayashi, and T. Shida, J. Chem. Phys. **108**, 7334 (1998).
4. H. Hoshina, M. Fushitani, T. Momose, and T. Shida, J. Chem. Phys. **120**, 3706 (2004).