ANOMALOUS MOBILITIES OF MOLECULAR IONS IN COOLED HELIUM GAS

H. Tanuma, H. Hidaka, S. Jinno, S. Matoba, M. Hananoe*, and K. Ohtsuki*

Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
*The University of Electro-Cimmunications, Chofu, Tokyo 182-8585, Japan

The dominant long-range ion-neutral interaction is the polarization potential which is in inverse proportion to the fourth power of the ion-neural distance. Because of this fact, the mobility of an ion in a gas generally approaches a finite constant value, which is called the polarization limit K_{pol}, as both an electronic field and temperature are lowered. However, more than ten years ago, we had found that the mobilities of CO^+ and O_2^+ in He at 4.3 K have much smaller values than K_{pol} in the low electric field region, and that of N_2^+ shows ordinary behavior. In order to understand this phenomenon, we had performed the mobility measurement for various molecular ions, i. e. NO^+, CH^+, CH_2^+, NO_2^+, CO_2^+, and CO_2^{2+}. Normalized mobility, which is defined as the ratio of reduced mobilities K_0 and K_{pol} is shown in Fig. 1 for five molecular ions. As the result of these experiments, it has been found that N_2^+ is only an exception.

To reveal the mechanism of this experimental finding, we had calculated the molecular ion mobility in He with the classical theories. It is necessary to obtain the interaction potential between the molecular ion and He atom for the calculation of the mobility. Therefore multi-reference SD-CI calculations using a *spdf* basis set were performed to obtain the potential energy surfaces for the N_2^+-He and O_2^+-He systems. Using the calculated potentials, we evaluated the momentum-transfer cross sections as a function of the collision energy with the classical trajectory method. Finally, by the calculation based on the two-temperature theory, we obtained the reduced mobility K_0 as a function of the effective temperature T_{eff} after the calculation of the collision integral $\bar{\Omega}^{(1,1)}$ which is the thermally averaged momentum-transfer cross section.

The experimental and calculated mobilities of O_2^+ in He gas are shown in Fig. 2. As can be seen in this figure, the reproduction by the theoretical calculation is satisfactory in this collision system. We analyzed each classical trajectory to find the reason why O_2^+ shows smaller mobilities than K_{pol} at the low T_{eff}. In the first half of the collision, the relative velocity is accelerated by the attractive potential between O_2^+ and He, and the rotational motion of O_2^+ is automatically excited due to the anisotropic interaction potential even if the collision energy is much lower than the lowest rotational excitation energy. In the very low collision energy, the kinetic energy of the relative motion becomes smaller than the depth of the potential well, and O_2^+ and He make a quasi-stable complex. This collision process resembles the quantal Feshbach resonance. In the latter half of the collision, the complex dissociates in the random direction and the rotational state returns to the initial one. This process does not change the relative energy, but the averaged velocity of O_2^+ in the initial direction is reduced by this type of collision. This mechanism has similarity with *the laser cooling*.

Because of such mechanism, the momentum-transfer cross section is enhanced to be much larger than the classical orbiting cross section, and the mobility becomes smaller than K_{pol}. This mechanism is also reproduced in the quantal calculation using wave packet propagation. By similar analysis, we found that the different behavior of N_2^+ is ascribed to small rotational rates due to the very isotropic potential energy surface.

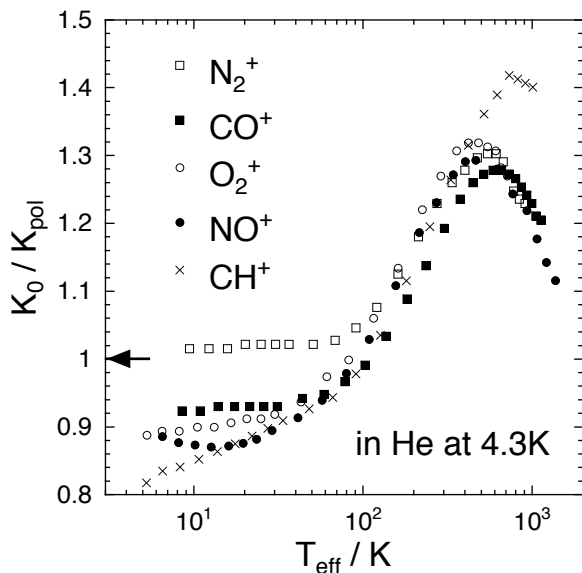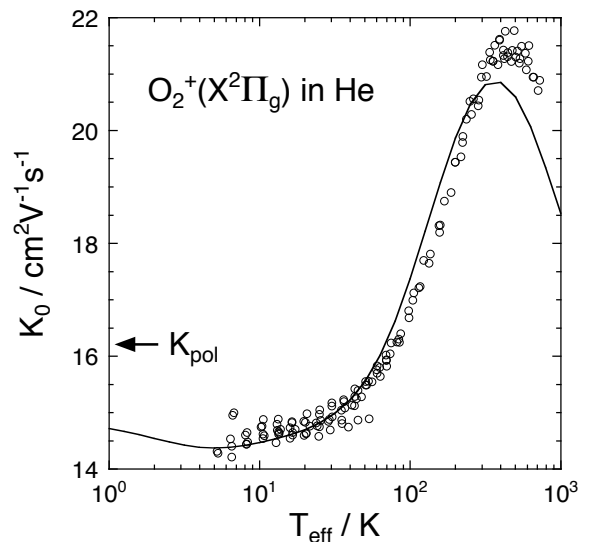Fig. 1. Normalized mobilities of five molecular ions in He gas at 4.3 K.

Fig. 2. Measured and calculated mobilities of O_2^+ in He gas at 4.3 K.