Separation of Electronic States and Isomers for Atomic and Molecular Ions in Cooled Gases by Ion Mobility Measurements

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The interaction potentials between the ions and the neutral gases determine the drift velocities of ions in gases. Because the interaction depends on the electronic state and geometrical molecular structure, the drift velocity can separate ion species beyond the mass analysis. This technique is applied for chemical analysis and is named *ion mobility spectrometry* as described in technical books [1,2,3]. On the other hand, the fundamental physics of ion mobility was developed in the 20th century and described in detail by pioneers of theoretical and experimental investigations[4].

We have developed an apparatus and measured the drift velocity v_d of various atomic and molecular ions in cooled helium gas at 77 and 4.3 K with liquid nitrogen and helium, respectively[5,6,7]. As we used an electron-impact ion source, metastable ions were produced in many cases, e.g., $C^+(2s2p^2\ ^4P)$ from CH_4 gas, and the separation from the ground state in the arrival time spectra was observed. Not only atomic ions but also molecular ions, e.g., NH^+ and NH_3^+, have two peaks corresponding to different electronic states in the spectra.

Recently, we performed experiments with hydrogen gas instead of helium gas. With the injection of H_2^+ into the drift tube filled with cooled H_2 gas, we have observed H_3^+ produced by the following ion-molecule reaction:

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$

The arrival time spectra of H_3^+ surprisingly split two components in weak electric fields. As the mobility of molecular ions depends on the molecular structure, we consider that two peaks correspond to the triangle and linear structures. The ground state of H_3^+ has a triangle structure confirmed with spectroscopic observation[8], and theoretical calculation proposes the first excited triplet state of linear structure. However, the energy level of this triplet state is too high to be produced in the low-energy collision of H_2^+ with H_2. Then, the meta-stable linear structure in the electrically ground state will be the candidate[9]. If this interpretation is correct, this result might be the first observation of linear H_3^+ in the laboratory.

With Li^+ injection at 77 K, we observed the formation of cluster ions, Li^+H_2, and measured the arrival time spectra. Here, the splitting into two peaks also indicates the unexpected existence of isomers, namely triangle and linear types.

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