Mobility of a Li$^+$ ion attached to 2-butanol in He gas

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Abstract.
The mobilities of a Li$^+$ ion attached to 2-butanol in He gas have been measured using a drift tube mass spectrometer at room temperature. We observed a significant reduction in the mobilities over the entire range of $E/N$.

1. Introduction
Experiments involving collisions of photons, electrons, and molecules with structurally complex molecular ions (such as organic molecular ions) in a gas phase have been performed in recent years to investigate interactions and cross sections. However, few studies have performed collision experiments involving complex molecular ions in the thermal energy region in a gas phase, as it is difficult to reduce the collision energy between an ion and a neutral below 1 eV due to the space-charge effect in the conventional ion beam method. Cross sections at low collision energies provide invaluable information on the behavior of molecular ions in the environment. The drift tube method is a powerful technique for studying ion–molecule collisions and for measuring gas-phase ion transport parameters, such as mobilities, diffusion coefficients, and reaction rate constants, at very low collision energies (i.e., from milielectronvolts to a few electronvolts). Ion mobility in a gas measured by the drift tube method is directly related to the momentum transfer cross section, which is determined by the interaction potential between an ion and a neutral. Therefore, the ion mobility provides not only the momentum transfer cross section at very low collision energies but also detailed information on the interaction potential.

It is necessary to measure the ion mobilities at a wide range of $E/N$ in order to obtain the information of the interaction potential. However, few measurements of the ion mobilities of complex molecular ions have been performed at a wide range of $E/N$, although a number of studies have been made on structure analyses for complex molecular ions using a drift tube method.

In this paper, we present the mobilities of Li$^+$ ion attached to 2-butanol($C_4H_{10}O$) in He gas at room temperature. A 2-butanol has two stereo-isomers of $(R)$-(-)-2-butanol and $(S)$-(+)-2-butanol. The mobilities of Li$^+$ (2-butanol) in pure He gas in this work are the basic data for giving the mobility of a chiral molecular ion in a chiral molecular gas with Blanc’s law.
2. Experimental setup

We have developed a drift tube for measuring ion mobilities and for observing ion–molecule reactions at room and liquid nitrogen temperature. The details of the experimental setup have been described elsewhere [1, 2]. We briefly mention only the important features and recent updates. The Li\(^+\) attachment ionization is used to produce Li\(^+\)(2-butanol) ions that ionize 2-butanol without producing fragment ions. The ions are mass-selected by a quadruple mass selector and are then injected into the drift tube with a kinetic energy of 9 eV. The injected ions are thermalized by collisions with a He buffer gas, and they drift under the influence of the uniform electric field in the tube. There are 13 guard rings inside the drift tube that generate the uniform electric field and six mesh electrodes that function as three electrical shutters for ions. These three shutters are mounted with a distance of 34 mm between the first and second gates and a distance of 25 mm between the second and third gates. A secondary electron multiplier detects the ejected ions from the drift tube after being analyzed by a Wien filter. The drift velocity is obtained from the slope of the arrival time between each shutter and the detector.

The ionization chamber and main chamber are pumped with turbo molecular pumps of 300 ℓ/s and 1100 ℓ/s, respectively, and a 4-inch oil diffusion pump is used to evacuate the detector chamber. The background pressures of the ionization, main, and detector chambers are approximately 5×10\(^{-3}\), 2×10\(^{-3}\), and 1×10\(^{-4}\) Pa, respectively, in typical operation with inner pressures of 30 Pa in the ion source and 70 Pa in the drift tube.

3. Results and discussion

The drift velocity \(v_d\) is proportional to the reduced electric field \(E/N\):

\[
v_d = n_0K_0\frac{E}{N},
\]

where \(N\) is the number density of the buffer gas molecules, \(n_0\) is the Loschmidt constant and the proportionality constant \(K_0\) is defined as the reduced mobility of an ion in a gas. \(K_0\) and \(E/N\) are in units of cm\(^2\)V\(^{-1}\)s\(^{-1}\) and Td (1 Td = 10\(^{-17}\) Vcm\(^2\)), respectively. On the assumption of an elastic collision and a central force potential, the mean collision energy \(\bar{\varepsilon}\) between ions and neutrals in a drift tube and the effective temperature \(T_{\text{eff}}\) are given by the Wannier’s equation [3]:

\[
\frac{3}{2}kT_{\text{eff}} \equiv \bar{\varepsilon} = \frac{3}{2}kT + \frac{1}{2}Mv_d^2,
\]

where \(k\) is the Boltzmann constant, \(T\) is the buffer gas temperature, and \(M\) is the mass of the neutral. Using \(T_{\text{eff}}\), we can make the comparison between the mobilities measured at different gas temperatures. In the classical transport theory of an ion in a gas [4], the momentum transfer cross section at very low collision energies is approximately given by the Langevin cross section, and the mobilities of atomic ions in monoatomic gases are close to the polarization limit \(K_{\text{pol}}\) in the limit \(E/N \rightarrow 0\) Td and the buffer gas temperature \(T \rightarrow 0\) K, which is given by

\[
K_{\text{pol}} = \frac{13.853}{\sqrt{\alpha \mu}} \text{ cm}^2\text{V}^{-1}\text{s}^{-1},
\]

where \(\alpha\) is the polarizability of the neutral in Å\(^3\) and \(\mu\) is the reduced mass between the ion and the neutral in atomic mass units.

The mobilities of Li\(^+\)(2-butanol) ions in He gas at room temperature are shown in Figure 1 as a function of (a) the reduced electric field \(E/N\) and (b) the effective temperature \(T_{\text{eff}}\).

The mobilities are independent of the buffer gas pressure and are slightly dependent on the reduced electric field \(E/N\). Notably, the values of the mobilities are significantly smaller than the polarization limit \(K_{\text{pol}} = 15.7\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) within the measurement range. Previously,
Figure 1. Mobilities of Li$^+$ (2-butanol) ion in He gas at 70 and 105 Pa at 305 K as a function of (a) reduced electric field $E/N$ and (b) effective temperature $T_{\text{eff}}$. The arrows indicate the polarization limit $K_{\text{pol}}$ at 15.7 cm$^2$V$^{-1}$s$^{-1}$.

Hidaka et al. and Sandersson et al. reported that the mobilities of small molecular ions in He gas at 4.3 K decrease less than $K_{\text{pol}}$ at a very low effective temperature of below 100 K [5, 6, 7]. Ohtsuki attributed the reduction in the mobilities of molecular ions to a Feshbach-like resonance due to the anisotropic potential energy surface between a molecular ion and a He atom predicted by classical trajectory calculations [8]. However, the reduction in the mobilities of the Li$^+$ (2-butanol) ion must be caused by a different mechanism because the mobilities do not rise above $K_{\text{pol}}$ even at high effective temperatures. Viehland et al. investigated the effect of the attractive and repulsive terms using the simple $(n, 6, 4)$ model potential [9] given as

$$V(r) = \frac{n\varepsilon_0}{n(3+\gamma) - 12(1+\gamma)} \times \left\{ \frac{12}{n} (1+\gamma) \left( \frac{r_m}{r} \right)^n - 4\gamma \left( \frac{r_m}{r} \right)^6 - 3(1-\gamma) \left( \frac{r_m}{r} \right)^4 \right\},$$

where $n$ is a parameter of the short-range repulsion energy, $\varepsilon_0$ is the depth of the potential minimum, $r_m$ is the position of the minimum, and $\gamma$ is a dimensionless parameter that is a measure of the relative strength of the $r^{-6}$ and $r^{-4}$ terms. The $r^{-6}$ term in the ion–atom interaction potential originates from the charge–induced-quadrupole interaction, the permanent-dipole–induced-dipole , and the fluctuating dipole–induced-dipole interaction, which is a part of the dispersion interaction. According to the calculations by Viehland et al., the addition of a sufficiently high $r^{-6}$ attraction energy can cause the mobilities to fall below the polarization limit $K_{\text{pol}}$ at all temperatures. Therefore, there is possibility that the reduction in the mobility of the Li$^+$ (2-butanol) ion is due to the large coefficient of the attractive $r^{-6}$ term in the interaction potential. However, there are other possible mechanisms, such as the effect of the anisotropic potential, the inelastic scattering, and so on. In order to understand the mechanism that causes the reduction in the mobilities of the Li$^+$ (2-butanol) ion, further studies are required, i.e., the measurements of the mobility at lower temperature and the quantum chemical calculation of the potential energy surface.
4. Summary
We measured the mobilities of Li\(^+\) (2-butanol) ions in He gas at room temperature using a drift tube mass spectrometer. The mobilities show lower values than the polarization limit over the entire measurement range.

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