Chemical reaction of sympathetically laser-cooled molecular ions

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We report an ion/neutral reaction of sympathetically laser-cooled molecular ions. Using laser-cooled fluorescence mass spectrometry, a reaction of about 100 sympathetically cooled H$_3$O$^+$ ions with NH$_3$ were traced at 4 min interval as the reacting ions were kept within a radio-frequency-quadrupole ion trap. To obtain the reaction rate of the reaction molecular dynamical calculation was used to relate the fluorescence mass spectra to the quantity of the molecular ions.


Ion trap multi-stage mass spectrometry (MS/MS) is a useful technique to identify molecular structures. Sample ions purified by resonant ejection of irrelevant ions are collisionally fragmented or chemical reacted with neutral gases in the spectrometer, and then the resulting product ions are detected mass-selectively. Ion trap MS/MS is applied to identify small amount of chemical compounds, DNAs, peptides, because it may require a smaller amount of samples than the other techniques such as x-ray diffraction and NMR. By nondestructive (or in situ) detection, the reactions can be traced using single ion-injection because the reacting ions can be preserved ions in the ion trap on every mass spectrometric stage. In Fourier transform mass spectrometers that use magnetic ion trap, molecular ions can be detected in situ with high sensitivity (~ single ion) by detecting induced current on the ion trap electrodes by trapped ions. In a radio-frequency-quadrupole (RFQ) ion trap, detection by induced current has not reached sensitivity comparable to that of ion ejection and detection. Thus, in conventional RFQ ion trap, multiple injections of ions are necessary when multi-stage fragmentation and ion/neutral reactions of unknown samples are traced because ions are lost from the ion trap in the detection process. To achieve highly sensitive nondestructive mass analysis of ions in an RFQ ion trap, sympathetic cooling, which is collisional heat exchange between laser-cooled ions trapped simultaneously, has been used. In 1996, ~80 sympathetically cooled molecular ions were mass analyzed using laser-cooled fluorescence mass spectrometry or LCF-MS, which suggested a possibility to trace molecular reactions in situ in a linear RFQ ion trap. Chemical reactions of laser-cooled magnesium ions and neutral hydrogen were observed in sympathetically cooled Wigner crystals.

In this letter, we show that LCF-MS can trace ion/neutral reactions of sympathetically cooled molecular ions in situ with high sensitivity. We believe this is the first observation of an ion/neutral reaction of sympathetically cooled molecular ions as a reactant. The observed reaction is

\[ H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O, \]

where the reactant ions H$_3$O$^+$ and the product ions NH$_4^+$ are sympathetically cooled by laser-cooled $^{24}$Mg$^+$ ions.

The laser-cooled fluorescence mass spectrometer is described in the previous report. About 100 H$_3$O$^+$ ions are created from H$_2$O and H$_2$ that are residual gases of the ultrahigh-vacuum (10$^{-7}$ Pa). H$_2$O$^+$ ions, which are produced from H$_2$O by electron impact, react with H$_2$ and with H$_2$O to produce H$_3$O$^+$ by 1 s. We introduced ammonia gas, whose partial pressure was monitored by a commercial quadrupole gas analyzer, through a variable leakage valve. The residual partial pressure of ammonia was 1.2±0.7×10$^{-9}$ Pa without ammonia gas introduction. For in situ LCF-MS, a dipole ac voltage is applied to the ion trap section, whose amplitude $v_{ac}$ is ~1 mV. The frequency is swept from high to low, or from low to high at sweep velocity is ±1.5 [kHz/s]. Inversely swept direction, the ions were lost (Fig. 1). We detuned the laser frequency for laser cooling by 10 MHz below the center of the absorption, which provides a high fluorescence rate and a moderate laser-cooling efficiency, so that trapped ions were in a gas phase because the cooling and rf heating were in balance. We monitored the phase of trapped ions by an image intensified CCD camera. Doppler profile of the fluorescence spectra suggested 10 K as the temperature of the gas phase ions.

Figure 2 shows repetitive fluorescence mass spectra observed in situ every ~4 min. The time indicated in the figure shows storage time elapsed between the initial ion loading and the start of each mass scan. Intensity changes of LIF at 246, 275 and 290 kHz show existence of ions with mass-to-charge ratio m/e=24, 19 and 18, because the intensity change at m/e=24 shows resonant excitation of the ions that have the secular frequency

\[ \omega_0 = \frac{eV_{ac}}{\sqrt{2m\Omega_0^2}}, \tag{2} \]

Because of Doppler broadening of the optical excitation spectrum of the laser-cooled ions, decreases of LIF intensity (or dips) at the optical resonance center represent increases of the temperature of the laser-cooled ions, and increases of LIF intensity (or peaks) represent decreases of the temperature of the laser-cooled ions. The dips at m/e=24 indicate direct excitation of the laser-cooled $^{24}$Mg$^+$ ions. The intensity change at m/e=18 and 19 imply excitation of NH$_4^+$ ions and H$_3$O$^+$ ions.
without peaks are observed because the temperature rise of the excited sample ions directly causes the temperature rise of the laser-cooled ions. We did not observe any peaks when the ions heavier than the laser-cooled magnesium ions were mass analyzed, nor xenon ions (m/e = 129–136) were analyzed by LCF-MS using laser-cooled barium ions (m/e = 138).

Line profiles at m/e = 18 and 19 in the present case are, however, asymmetrical with peaks, which are also observed in the previous report. Increase of fluorescence indicates that we cannot assume simple positive correlation between the temperature of the sample ions and the temperature of the laser-cooled ions. Therefore, we cannot use the strong coupling model, and hence the equivalent width, to estimate the amount of the ions from the line profile.

The efficiency of sympathetic cooling was discussed by T. Baba and I. Waki. Sympathetic cooling rate of sample ions with mass m_i, where laser-cooled ions have mass m, is proportional to

\[ k \propto \frac{2m(m_i - em)}{(m_i + m)^2}. \]  

For a linear ion trap, the rf coupling constant \( e \) is 0.533 for \( q \leq 0.5 \). Ions with m/e = 18 and 19 can still be sympathetically cooled because the mass is heavier than 0.533 m. The efficiency for m/e = 18 and 19, however, decrease to a half of the efficiency for m/e = 29. Therefore, m/e = 18 and 19 ions are weakly coupled to laser-cooled ions, which is consistent with the deviation from the strong coupling model in our observation of increase of fluorescence at m/e = 18 and 19.

To relate the amount of ions to the complex line profile at m/e = 18 and 19 in the weak-coupling case, we tried to explain LCF-MS spectra by molecular dynamical (MD) calculations. We describe the linear ion trap field as follows:

\[ \psi(x, y, z) = \frac{V_{rf}}{2r_0^2}(x^2 - y^2)\cos \Omega t + \frac{\Delta V}{z_0^2} \left( z^2 - \frac{x^2 + y^2}{2} \right). \]

Here, the first term on the right-hand side represents the ion trap rf field and the second represents a harmonic dc field to confine the ions in the z direction. \( \Delta V/z_0^2 \) represent the strength of the dc potential. We use conventional formulas for laser cooling and Coulomb forces. We apply a supplemental ac field for mass analysis,

\[ V_{ac} = v_{ac} \frac{x + y}{\sqrt{2r_0}} \cos \omega t. \]

Figure 3(A) shows a MD calculation of in situ LCF-MS when we trap 30 laser-cooled \( ^{24}\text{Mg}^+ \) ions and 15 m/e = 18 ions. First, using MD, we obtained an equilibrium state where the laser cooling and rf heating are in balance in the absence of the supplemental ac field. After the equilibrium has been reached, the supplemental ac field with \( v_{ac} = 1 \) mV was applied, whose frequency is shown in the horizontal axis of Fig. 3(A). The frequency of the ac field was fixed rather than swept because MD calculations for a sweep take a long...
One of characteristics of LCF-MS is that the sample ions are sympathetically cooled. This may realize observation of much cooler ion–molecular reactions than the conventional observation with ~1 Kelvin using cryogenic traps, which show quantum tunneling through shallow reaction potentials. In this work, the reaction temperature is ~100 K because the neutral ammonia gas is at room temperature.

FIG. 3. Molecular dynamic calculation of LCF-MS. (A) Reproduction of a fluorescence mass spectrum with a peak. The thick solid line shows the fluorescence intensity emitted by the laser-cooled ions. The thin solid line denoted $T_s$ shows the kinetic energy of the sample ions and the dashed line denoted $T$ shows the temperature of the laser-cooled ions. (B) Signal intensity at the m/e=18 ions vs the amount of the m/e=18 ions when the m/e=18 ions are excited by the supplemental ac field for mass analysis.

FIG. 4. (A) Signal variation of the m/e=18 and 19 ions in Fig. 2. Reaction speed of the m/e=19 ions to the m/e=18 ions is 340 s (1/e) by exponential fitting. (B) Reaction speed of the m/e=19 ions to the m/e=18 ions vs the partial pressure of NH$_3$ gas in the ultra-high vacuum chamber. The rate constant is calculated as 2.2±0.2×10^{-9} [cm$^3$/s].
To observe cold ion/neutral reactions using LCF-MS, we should use cooled neutrals such as cryogenically cooled hydrogen,\textsuperscript{21,22} laser-cooled atomic gases,\textsuperscript{23} and NH\textsubscript{3} cooled by a Stark decelerator.\textsuperscript{24}

Can sympathetic cooling cool vibrational and rotational states of molecular ions? We do not have any information about the internal degrees of freedom of the sympathetically cooled molecules, because it is very difficult to observe fluorescence emitted by the molecules because of optical pumping to vibrational and rotational states as well as small number of trapped ions in the ion trap. If the measurement is possible using some proposed methods for molecular laser-cooling,\textsuperscript{25–27} which may be applicable to spectroscopy of molecules. It is very interesting because it could realize control and monitoring of the internal degree of freedoms to construct a molecular quantum computer like a NMR quantum computing.\textsuperscript{28}

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\textsuperscript{16} Definition of the rf coupling constant \(\tilde{e}\) of a Paul trap was originally given by Y. Moriwaki \textit{et al.}, Jpn. J. Appl. Phys. \textbf{31}, L1641 (1992).