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A selected ion flow tube apparatus has been modified to include a well-defined flow drift region and instrumentation for ion modulation and data acquisition. This apparatus was used to measure the first experimental mobilities for several important families of atmospheric cluster ions. Core ions include the nitric oxide cation, ammonium ion, and hydronium ion; solvating ligands include water, ammonia, acetonitrile, and acetone. Several collision gases were examined including helium and nitrogen, as well as the polar gases, water and acetone. The mobilities of prototypical aromatic species have also been measured and evaluated to distinguish between isomeric structures.

Doppler-resolved laser-induced fluorescence measurements of collision-induced rotational alignment of the molecular nitrogen cation drifted in helium have been carried out. A strong correlation was found between the degree of rotational alignment and the velocity subgroup probed along the field direction; the correlation between alignment and velocity increases with increasing field strength. These results are attributed primarily to the change in anisotropy of the relative velocity vector distribution of the nitrogen cation-helium pair with field strength.

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Final Technical Report
"Reactions of Atmospheric Cluster Ions"
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A. Mobilities of Cluster Ions

Cluster ions play an important role in the ion chemistry of the earth's atmosphere. For example, clusters with NO^+, H_3O^+ and NH_4^+ as core ions, and with H_2O, NH_3 or CH_3CN as solvating ligands, among many others, have been detected in the earth's troposphere, stratosphere and ionosphere. Although the association and dissociation processes forming these ions are in general well-understood, the mobilities of these cluster ions remain largely uncharacterized. These values are essential, not only in modeling atmospheric phenomena, but also in providing direct information about the ion-buffer gas interaction potential.

Our selected ion flow tube apparatus has been modified to include a well-defined flow drift region and instrumentation for ion modulation and data acquisition. Core ions are generated in an ion source, mass-selected and injected into the flow tube where they associate with added solvent molecules before entering the drift region. Two drift rings, at known separation, are simultaneously pulsed; the resulting ion depletions are detected with a quadrupole mass filter in a time-resolved manner, as a function of E/N. Under sponsorship of the AASERT program, we have completed studies of the mobilities of two important families of atmospheric cluster ions, $NO^+(CH_3CN)_n$ and $NH_4^+(NH_3)_n$ (n=0-3), and of several prototypical aromatic species. We have also explored the mobilities of ions and cluster ions drifting in polar gases.

1. Mobilities of $NO^+(CH_3CN)_n$ Cluster Ions

The mobilities of $NO^+(CH_3CN)_n$ cluster ions (n=0-3) drifting in helium and in mixtures of helium and acetonitrile (CH_3CN) have been measured in the SIFT-drift instrument [*J. Chem.*

Phys. **105**, 10398 (1996)]. The mobilities in helium decrease with cluster size, as shown in Table 1, and depend only weakly on the characteristic parameter E/N. The size dependence is explained in terms of the geometric cross sections of the different cluster ions. The rate constants for the various cluster formation and dissociation reactions have also been determined in order to rule out the possibility that reactions occurring in the drift region influence the measurements in the mixtures. In addition, several experiments were carried out in a flowing afterglow source-SIFT-drift instrument (FA-SIFDT), in which mass-selected cluster ions can be injected for study in pure helium. These measurements provided a consistent set of results.

Since high pressures of acetonitrile are required to form $NO^+(CH_3CN)_2$ and $NO^+(CH_3CN)_3$, the mobilities of these ions are found to be dependent on the acetonitrile concentration, as a result of anomalously small mobilities of these ions in acetonitrile. These mobilities are deduced using Blanc's law and are summarized in Table 1.

Table 1. Reduced zero-field mobilities ($cm^2\,V^{-1}\,s^{-1}$) of $NO^+(CH_3CN)_n$ in collision gas M at 300K

M	n=0	n=1	n=2	n=3
He	22.4 ± 0.5	12.3 ± 0.3	8.2 ± 0.2	7.5 ± 0.5
CH_3CN			0.041 ± 0.004	0.044 ± 0.004

These values are at least an order of magnitude smaller than any previously reported ion mobility, which can be partly explained by the large ion-permanent dipole interaction between the cluster ions and acetonitrile. The remaining discrepancies may be the result of momentum transfer outside the capture cross section, dipole-dipole interactions, ligand exchange, the formation of long-lived collision complexes or the transfer of kinetic energy into internal energy of the cluster ion and acetonitrile molecule.

2. Mobilities of $NH_4^+(NH_3)_n$ Cluster Ions

Ammonia and its cluster ions have been detected in the earth's troposphere, the lowest 10-15 km of the earth's atmosphere. We have studied the formation and dissociation kinetics of the $NH_4^+(NH_3)_n$ cluster ions and demonstrated that these reactions do not affect the mobility measurements. Experiments were carried out using both SIFDT and FA-SIFDT instrumentation, and the results are in good agreement. Although the dipole moment of NH_3 (1.471 D) is smaller than that of CH_3CN (3.924 D), the mobility values of the cluster ions were found to depend on ammonia concentration. Therefore, zero field mobilities both in helium and in ammonia were determined and are summarized in Table 2 [*J. Chem. Phys.* **106**, 530 (1997)].

Table 2. Reduced zero-field mobilities ($cm^2\,V^{-1}\,s^{-1}$) of $NH_4^+(NH_3)_n$ in collision gas M at 300K

M	n=0	n=1	n=2	n=3
He	22.1 ± 0.4	16.6 ± 0.4	12.2 ± 0.4	12.1 ± 0.4
NH_3	0.94 ± 0.35	0.83 ± 0.22	0.50 ± 0.27	0.25 ± 0.20

3. Mobilities of Aromatic Ions

We have determined the mobilities of several prototypical aromatic ions drifting in helium, including $C_6H_5^+$ [11.7 ± 0.4 $cm^2\,V^{-1}\,s^{-1}$], $C_6H_6^+$ [11.8 ± 0.3 $cm^2\,V^{-1}\,s^{-1}$], $C_6H_7^+$ [11.6 ± 0.4 $cm^2\,V^{-1}\,s^{-1}$], $C_{12}H_{12}^+$ [7.6 ± 0.3 $cm^2\,V^{-1}\,s^{-1}$] $C_{12}H_{11}^+$ [7.8 ± 0.3 $cm^2\,V^{-1}\,s^{-1}$], naphthalene cation ($C_{10}H_8^+$) [8.8 ± 0.3 $cm^2\,V^{-1}\,s^{-1}$], and biphenyl ($C_{12}H_{10}^+$) [7.6 ± 0.3 $cm^2\,V^{-1}\,s^{-1}$] [*J. Phys. Chem.* **100**, 14908 (1996)]. These results demonstrate that the compact rigid structure of the naphthalene cation is readily distinguished from the more bulky, less rigid structures of the biphenyl cation and of the benzene dimer cation. In addition, calculated mobilities suggest that, for the benzene dimer cation, the sandwich structure is slightly favored over the axial T-type structure.

4. Mobilities of Ions in Helium - the Hard Sphere Collision Model

Angle-averaged hard sphere collision cross sections have been calculated from the geometric structures of the cluster ions described above as well as for the $H_3O^+(H_2O)_n$ system. These values have been used to compute the zero-field mobilities of the cluster ions in helium [*Int. J. Mass Spectrom Ion Processes*, in press, 1997]. As shown in Fig. 1, the predicted mobilities, indicated by the solid curve, are in good agreement with the experimentally measured values. Ion-induced dipole interactions, indicated by the dashed line, are important only for the smallest ions drifting in helium.

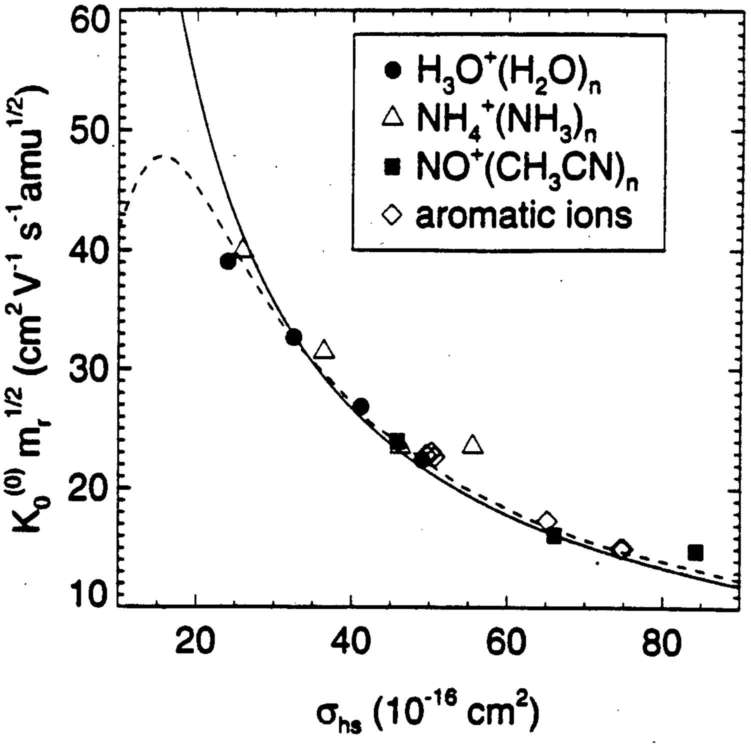

Figure 1. Cluster ion mobilities in He at 300 K vs. the angle-averaged hard-sphere cross section of the ions. The solid curve represents the hard-sphere collision model; the dashed curve includes ion-induced dipole attraction.

5. Mobilities of Ions in Polar Gases

The mobility of ions drifting in polar gases is an intriguing but relatively unexplored area; our SIFDT experiments have provided important new results and understanding. We have recently extended a number of theoretical models which describe capture in ion polar-molecule collisions to the calculation of ion mobilities [*J. Chem. Phys.* **106**, 5937 (1997)]. The model specifically addresses the ion-dipole (μ) interaction, which makes a large contribution, as well as the ion-polarizability (α) interaction. Figure 2 demonstrates that reasonable agreement is obtained between these calculated mobilities and the available experimental data. Remaining discrepancies may be due to the failure of the capture cross section to describe the momentum-transfer cross section, dipole-dipole interactions, ligand-exchange reactions, inelastic collisions and the validity of Blanc's law.

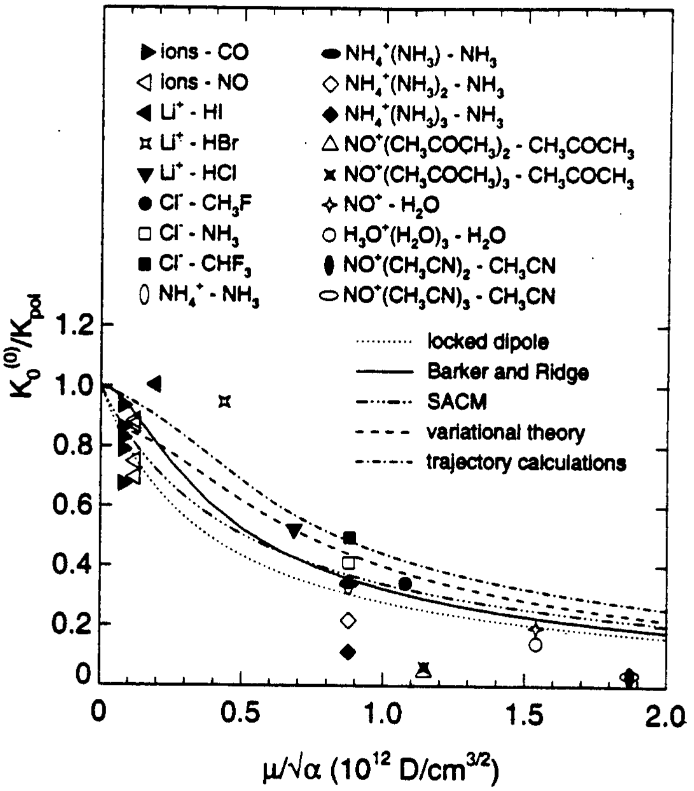

Figure 2. **The ratio between the measured and calculated zero-field mobilities $K_0^{(0)}$ and the polarization limit K_{pol} as a function of the parameter $\mu/\sqrt{\alpha}$ at 300 K.**

B. Laser Doppler Probing of Ion Alignment

Under sponsorship of the AASERT program, we have completed Doppler-resolved laser-induced fluorescence measurements of collision-induced rotational alignment of $N_2^+(v''=0)$ drifted in helium [*J. Chem. Phys.* **106**, 5413 (1997)]. We employed a single frequency ring dye laser to probe the $R_1(N''=15)$ rotational line of the B $^2\Sigma_u^+$ - X $^2\Sigma_g^+$ system both parallel and perpendicular to the drift field at three different field strengths and at several different Doppler-selected velocities. A strong correlation was found between the degree of rotational alignment and the velocity subgroup probed along the field direction. For field strengths of 8 and 16 Td and laser probe parallel to the drift field, there is a monotonic increase in the quadrupole alignment parameter $A_0^{(2)}$ with higher velocity subgroup, up to a maximum value of $A_0^{(2)} = -0.150$ (6) for 16 Td at the high-velocity tail. There is evidence that the correlation between alignment and velocity increases with increasing field strength. These results are attributed primarily to the change in anisotropy of the relative velocity vector distribution of the N_2^+-He pair with field strength.

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