

## PROBING COLLISIONAL EXCITATION IN ION-MOLECULE COLLISIONS BY FLUORESCENCE DETECTION

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High energy ion-molecule collisions are common in the atmosphere. Species such as oxygen, nitrogen, helium and neon fluoresce upon collisions with... leading to aurora. In mass spectrometry, keV ion-molecule collisions are used in CID to cause fragmentation of ions resulting in useful structural information. The deposition of internal energy in the ions during keV collisions, however, is not well understood. A possible way to study this is by coupling fluorescence detection with mass spectrometry.

The goal of this project is to investigate how ions and molecules are excited by observing the emission of photons from excited-state species. Ion-molecule collisions are carried out under normal CID conditions in a modified VG ZAB mass spectrometer. A spectrograph and a CCD camera for collecting photon emissions are installed above a collision cell. The spectra give information on the electronic state of both precursor and fragment species that are formed upon collisional excitation. A set of electrostatic lenses installed before and after the collision cell allow the ion translational energy to be varied between 500 and 8000 eV.

The fluorescent spectrum (190-1020 nm) of an 8 kV  $N_2^+$  ion beam colliding with He results in several types of emissions:  $N_2^+ B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$  ( $\Delta v = 2, 1, 0, -1, -2$ ) emission band and several emission lines from He, N and  $N^+$ . Preliminary studies of photon emissions with respect to ion translational energies show that the relative intensities of the  $N_2^+ B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$  emission band is not altered by ion translational energy. This result is consistent with a curve-crossing mechanism for collisional excitation. As the collision complex is formed, there is a probability that the ground state complex will curve-cross with an excited state of the complex, which upon dissociation yields the ion in an excited state. The probability that the crossing occurs decreases with increasing lifetime of the complex (and hence with decreasing ion translational energy), but the total amount of energy deposited remains the same. The fluorescence spectrum of an 8 kV  $He^+$  ion beam colliding with  $N_2$  also shows the  $N_2^+ B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$  emission band as a result of favourable charge transfer ( $\Delta H = -9.01\text{eV}$ ). The relative intensities of the emission bands, however, are remarkably different from the reverse experiment described above. Collisions of  $N_2^+$  with  $O_2$  also result in favourable charge transfer reaction ( $\Delta H = -3.51\text{eV}$ ). This results in much lower intensities from the  $N_2^+$  emissions. Interestingly, we also observe the  $b^4\Sigma_g^- \rightarrow a^4\Pi_u$  emission band from  $O_2^+$ . The neutralization energy balance is not enough to excite  $O_2^+$  to the b state in this case. The rest of the energy must result from the conversion of ion translational energy. The above cases indicate the possibility of studying ion-molecule collisions including charge-transfer reaction by fluorescence detection on a mass spectrometer.