Electronic Energy Transfer in a Collinear Expansion:

$Xe*(^3P_2) + N_2 \rightarrow Xe + N_2*(W\ ^3\Delta_u,\ B\ ^3\Pi_g,\ A\ ^3\Sigma_u^+)$

Prof. Ceyer,

An original plan for experiments in our lab was to optically pump $Hg*(^3P_2)$ atoms using a two-photon transition and use the metastable atoms to produce triplet acetylene by collisional energy transfer during co-expansion in a free jet. The Hg* and C_2H_2* metastables were to be detected by electron ejection from a gold surface (work function 5.1 eV).

Wilton and I decided to use the Xe* + N_2 system as a test case for acetylene, because the lowest excited state energies for these systems are well above the work function of gold. Also, the two-photon transition to optically pump $Xe*(^3P_2)$ is at a convenient wavelength for our lasers. Additionally, any nitrogen initially prepared in the B $^3\Pi_g$ state is readily observed by fluorescence to A $^3\Sigma_u^+$. The A $^3\Sigma_u^+$ state, in turn, has an extremely long lifetime, so this technique offers an opportunity to "preview" the production of SEELEM-detectable N_2* metastables using fluorescence.

Although we recorded strong signals and made several interesting observations in both LIF and SEELEM for this system, we decided to move on to the Hg* + C_2H_2 reaction; it remained our goal to obtain new and detailed information on the acetylene triplet states. However, developments in recent months have renewed our interest in the Xe* + N_2 system. In this brief note, I'll focus on a particularly intersting dataset from 2006 and discuss it in light of our current results.

2006 Experiments

One of the most intriguing observations from our first round of experiments was the SEELEM time-of-flight spectrum recorded using a small amount of xenon in a beam of nitrogen (see figure 0-2). A transformation of this TOF profile into velocity space is suggestive of forward-scattered N_2* with vibrational structure.

Figure 0-3 shows the velocity profile corresponding to the TOF profile in figure 0-2. In the plots, a flight distance of 30cm was used to determine the velocity, and

the SEELEM intensities were corrected for the volume of velocity elements after the transformation. The large peak with velocity 485 m/s can be assigned to Xe* with a translational temperature of 14K, as shown in the top panel. The smaller peak at 770 m/s can be fit to a velocity profile of N_2 with the same translational temperature, 14K.

We know from other experiments that a neat molecular beam of acetylene (having the same mass as nitrogen) travels with a mean flow velocity of approximately 800 m/s in our apparatus. From experiments with 50:50 mixtures of nitrogen and xenon, we know that the xenon metastable peak shifts only slightly from its velocity in neat xenon, which is close to the value presumed here.

Making the somewhat adventurous assumption that the peaks discussed above correspond to Xe* and N_2 moving at their respective mean flow velocities in the beam, we can convert to a center-of-mass coordinate system. Figure 0-4 shows a center-of-mass velocity profile generated with these assumptions. Potential curve-crossing models of the Xe*($^3P_2$) + N_2 reaction indicate that N_2* molecules formed in $v' = 4, 3, 2$ of the B $^3\Pi_g$ state will accumulate translational energy as they exit the reaction on the product potential surfaces (the translational energy arises in a classical sense from electrostatic repulsion between the product species) [1].

On the figure, bars have been placed at N_2 velocities which correspond to a full conversion of the reaction exothermicity into forward velocity of the N_2 products. For example, the $v' = 4$ level of the nitrogen B $^3\Pi_g$ state lies 1113 cm^{-1} below the energy of Xe*($^3P_2$). For N_2* produced in this level, the limiting forward velocity of the scattered product molecules is 975 m/s ($= \sqrt{2E/m}$). In this instance, the effect of backscattered Xe* was not included, so the location of these bars slightly exceeds the real limit for N_2* translational energy.

The center-of-mass transformed profile shows a peak of metastable intensity that falls off near the $v' = 4$ limit for N_2*(B $^3\Pi_g$). This suggests that we may be observing forward-scattered N_2 products with vibrational structure. A similar effect is not present for the $v' = 3, 2, 1$ levels of this electronic state.

Another interesting aspect of forward-scattered N_2* is that, if an isotropic dis-

tribution of products is assumed, the SEELEM detector covers a solid angle of less than 0.1% of the entire area of scattered products. Taking this factor into account, the total intensity of N_2* observed in forward scattering may be much larger than it appears in our profiles.

2007/08 Experiments

The major problem with our previous round of experiments was the possible presence of ions in the SEELEM time-of-flight profiles. A N_2^+ or Xe^+ ion contains internal energy well in excess of that needed to eject an electron from a gold surface.

In December 2007, Erika Robertson designed and constructed a simple ion deflector for our chamber. This deflector consists of two parallel screens separated by ~2cm and positioned parallel to the beam. A low voltage (around 10V) is sufficient to produce a repeatable TOF profile which we believe is free from ion signal.

The most recent time-of-flight profiles recorded under similar conditions to the above dataset do not contain any metastable signal above the limit for N_2*(B $^3\Pi_g$), $v' = 4$. Thus, we conclude that the signal above a laboratory velocity of 1000 m/s in the above dataset is due to ions.

Within the N_2 peak observed in the present datasets, there may also be some structure related to close-lying vibrational levels of the W $^3\Delta_u$ and A $^3\Sigma_u^+$ electronic states. This is presently under investigation by my colleagues.

– Kyle (March 2008)

[1] Ch. Ottinger, A.F. Vilesov, and D.D. Xu. *Chemical Physics* **192**, 49 (1995).

Figure 0-1: Vibrational energy levels and potential curves for N_2^* W $^3\Delta_u$, B $^3\Pi_g$, and A $^3\Sigma_u^+$. The x-axis is the radius of separation between the nitrogen atoms in N_2, in units of Angstroms. The y-axis is potential energy in electron volts. The W $^3\Delta_u$ and A $^3\Sigma_u^+$ states of nitrogen are metastable, while the B $^3\Pi_g$ state decays by fluorescence to A $^3\Sigma_u^+$, with an average lifetime of several μs. Also shown in the figure is the metastable $^3P_2$ level of Xe, which lies close in energy to the $v = 5$ level of N_2^* B $^3\Pi_g$, the $v = 5$ level of W $^3\Delta_u$, and the $v = 14$ level of A $^3\Sigma_u^+$. From Krümpelmann, T. PhD Dissertation, MPI für Strömungsforschung, Göttingen (1987).
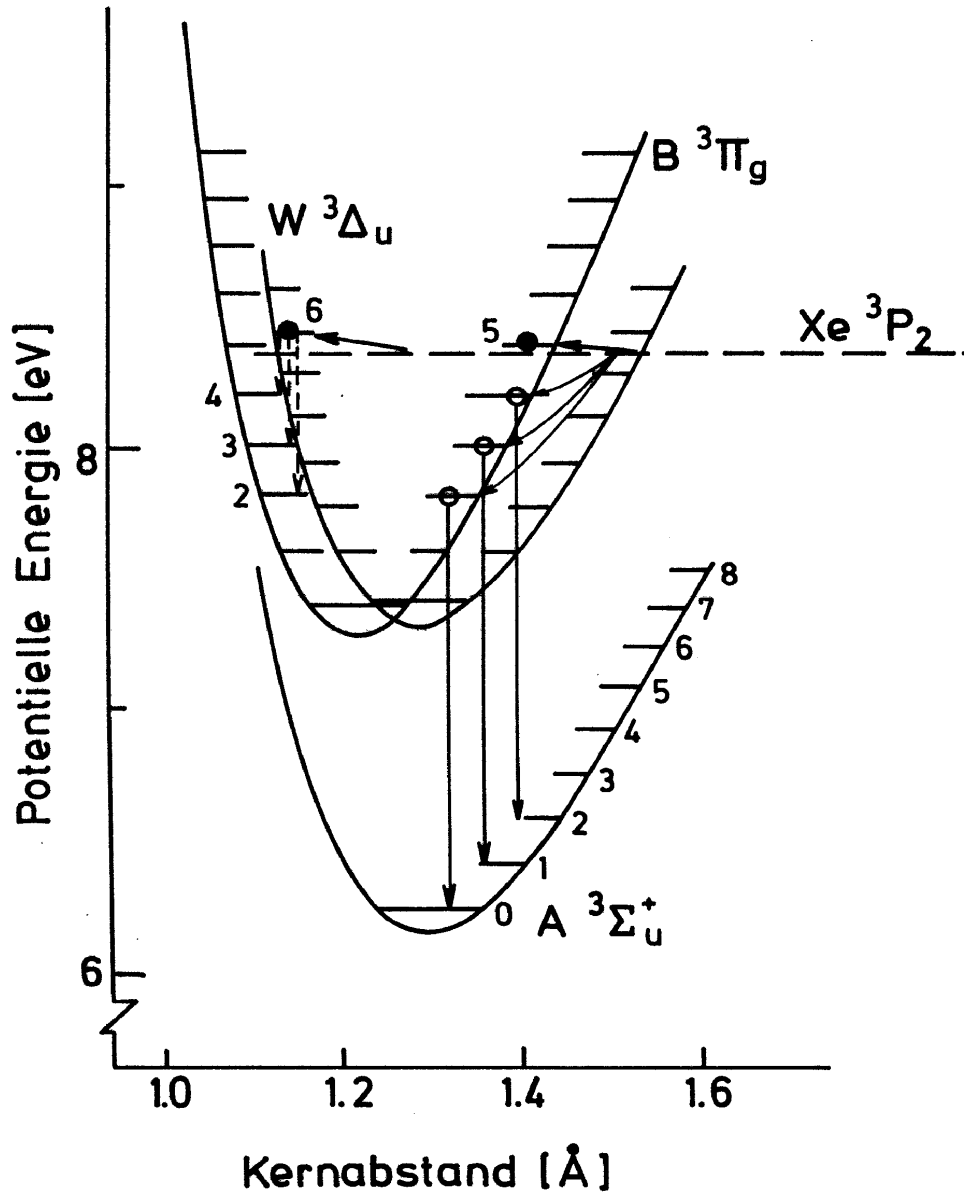
Figure 0-2: Time-of-flight arrival of Xe* and N$_2$* metastables detected by SEELEM. The gas mixture is mostly nitrogen ($P_b = 24\,psi$), with residual xenon left in the nozzle from a previous experiment.

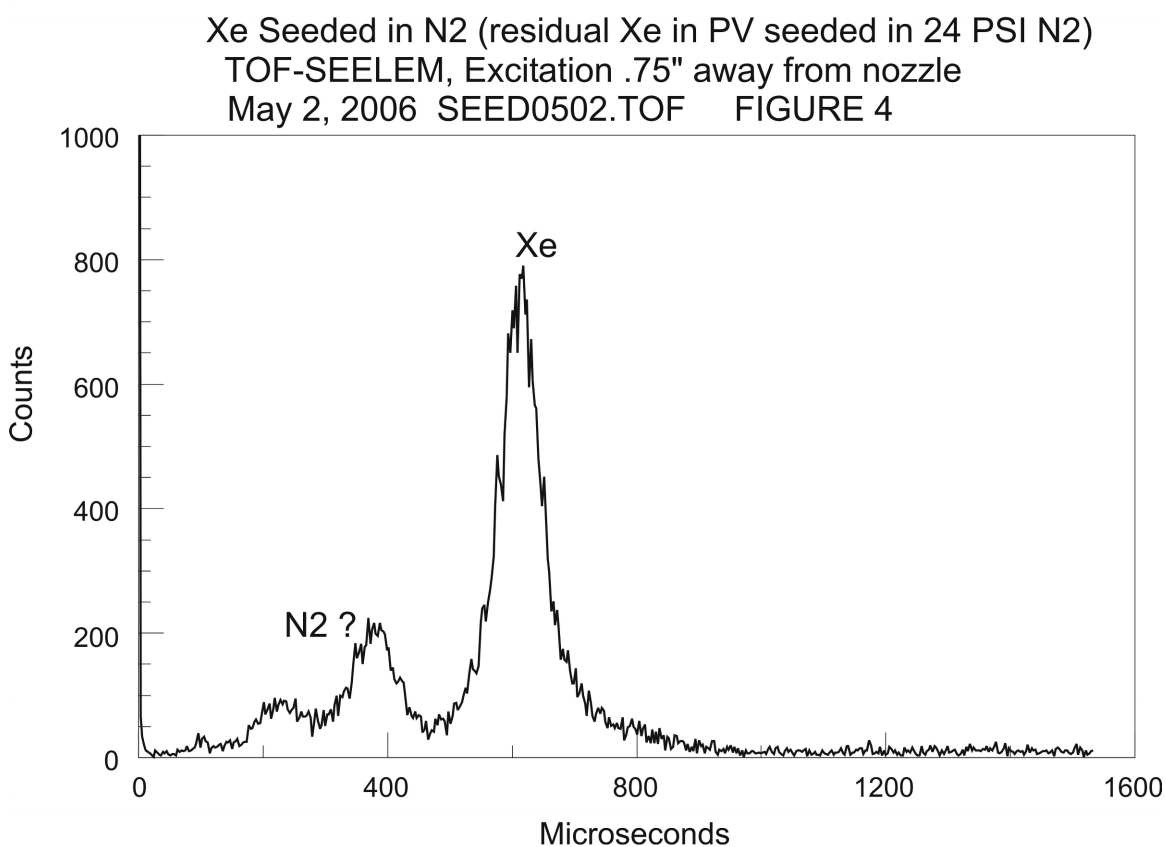Xe Seeded in N2 (residual Xe in PV seeded in 24 PSI N2)
TOF-SEELEM, Excitation .75" away from nozzle
May 2, 2006 SEED0502.TOF   FIGURE 4

Figure 0-3: Laboratory-frame velocity profiles of Xe* and N_2* metastables detected by SEELEM, transformed from the data in figure 0-2. The experimental data in both plots is identical. The top plot is overlayed with a velocity distribution of Xe atoms having a translational temperature of 14K and a mean velocity of 485 m/s. The bottom plot is overlayed with a velocity distribution of N_2 molecules having the same temperature and a mean velocity of 770 m/s.

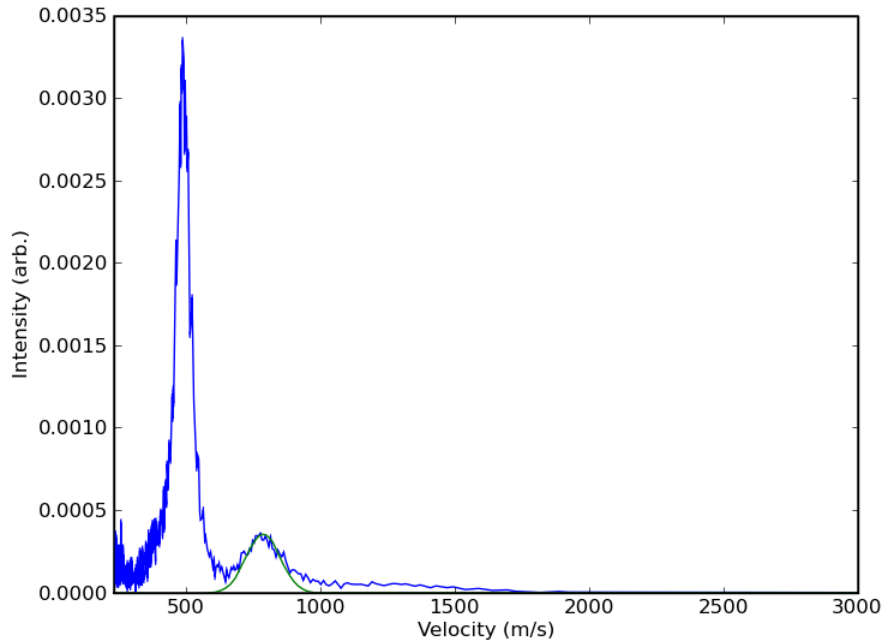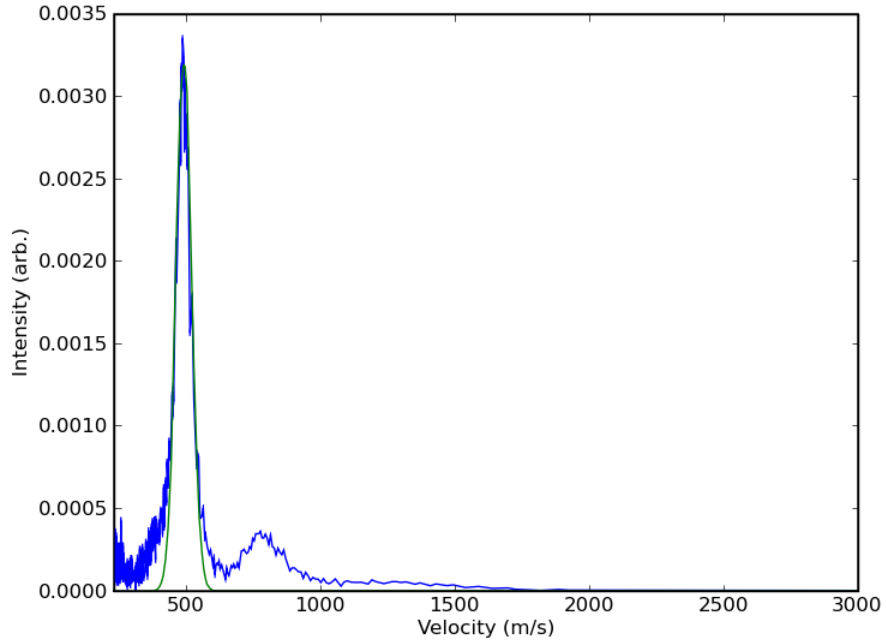Figure 0-4: Center-of-mass velocity profile of metastable species produced by colli-sional excitation transfer between Xe*($^3P_2$) and N_2 after co-expansion in a free jet. The plot is marked with bars that indicate the limit of forward-scattering velocity for N_2 in the $v = 4, 3$ levels of the B $^3\Pi_g$ state.

7