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The AFOSR/AASERT research efforts over this past year have been toward the following two thrusts: i) state-to-state collisional energy transfer in H_2O, HF and CH_4 in crossed molecular beams via high sensitivity, direct absorption of a single mode IR probe laser, ii) development and testing of high resolution IR laser Dopplerimetry methods for measuring velocity and quantum-state resolved Cl + HCl scattering in open shell collision systems.

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TITLE:	State-to-State Collisional Dynamics of Atmospheric Species
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JUNIOR RESEARCH PERSONNEL:	Bill Chapman (AASERT)

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Achievements under the AFOSR/AASERT program grant have been in the following two areas. i) We have continued to refine methods for state-to-state collisional energy transfer in crossed molecular beams, based on high sensitivity direct IR laser absorption, and allowing absolute cross sections to be obtained by measurement of absolute number densities of the scattering species (CH_4, H_2O, HF with rare gases). ii) We have developed a new capability for measuring state-resolved energy transfer in "hot atom" collisions of open shell radicals, and applied this to a study of Cl + HCl(J). By absolute absorbance measurements and analysis of high resolution Doppler profiles, absolute integral cross sections for state-resolved collisional loss from and gain into a specific final J state are obtained.

1) As a major focus of the AASERT program during the past year, we have continued to refine and exploit high resolution IR methods for monitoring state-to-state collisional energy transfer in low density, crossed supersonic jets. The method involves i) supersonic cooling of the IR absorber into a well defined initial rotational state, ii) scattering from this state into various final states by collisions with a second supersonic jet, and iii) probing the final state distribution by fractional absorption of tunable F-center laser light in the intersection region of the two expansions. By virtue of dual beam subtraction, the IR detection sensitivity ($\lesssim 10^{-6}/\sqrt{Hz}$) is sufficiently high to observe collisionally excited species present at the low densities needed to ensure single inelastic collision conditions. The high resolution (0.0001 cm^{-1}) of the IR probe laser offers 3 to 5 orders of magnitude improvement in quantum state-selection/detection over current time-of-flight methods that probe kinetic energy loss distributions in the scattered flux.

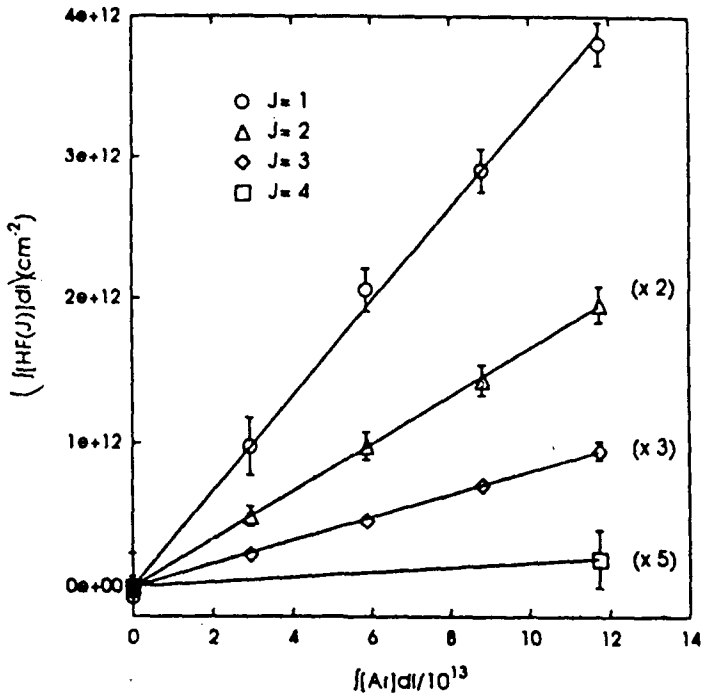

Figure 1

We have performed state-resolved scattering studies for HF colliding with rare gases. First, the relative cross sections for scattering from $J=0$ to $J=1$, 2, 3, and 4 are determined by monitoring the integrated absorbances for P(J) lines as a function of backing pressure. Sample data are shown in Fig. 1 for collisions of Ar with HF($J=0$) at center of mass energies of 400 cm^{-1}, and which verify the anticipated linear dependence on collider number density. Relative state-to-state collision cross sections are obtained from the slope ratios for the various curves, as shown in Fig 2. These experimental values can be tested against theoretical predictions from QM full close coupling calculations, based on a "trial" ArHF potential surface determined by Hutson from van der Waals data. The agreement (see Fig. 2) with theory is quite good, though there are small differences that are outside the error limits. We are making similar studies of rare gas collisions with para (0_{00}) and ortho (1_{01}) H_2O, which also permit comparison with recently developed potentials (e.g., the Ar-H_2O surface of Cohen and Saykally) derived from high resolution spectroscopy in the bound state region. These studies are highlighting an important question of how accurately the repulsive wall anisotropies at $E>0$ are determined from spectroscopy in the van der Waals region at $E<0$.

One advantage of a high resolution IR probe technique is that <u>absolute</u> number densities in the scattering region can be directly determined from the fractional absorbances and known IR line strengths. Specifically, by "doping" the scattering beam with trace amounts of an IR absorber, the column integrated scattering densities (integrated over the multipass region) can be reliably determined. As one example, inelastic scattering data for Ar + H_2O out of the lowest "para" ($J_{K_aK_c} = 0_{00}$) and "ortho" ($J_{K_aK_c} = 1_{01}$) levels are shown in Fig. 3. The plot indicates the total loss of the initial quantum state (column integrated densities) as a function of stagnation pressure of the

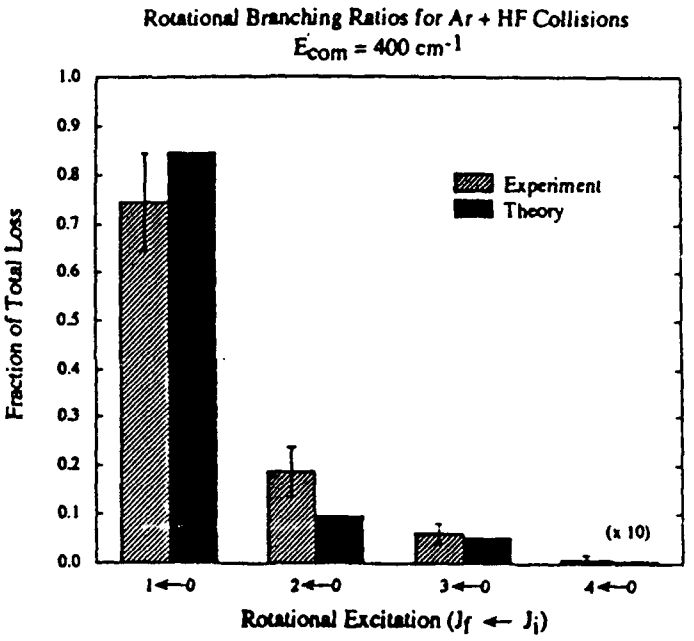

Figure 2

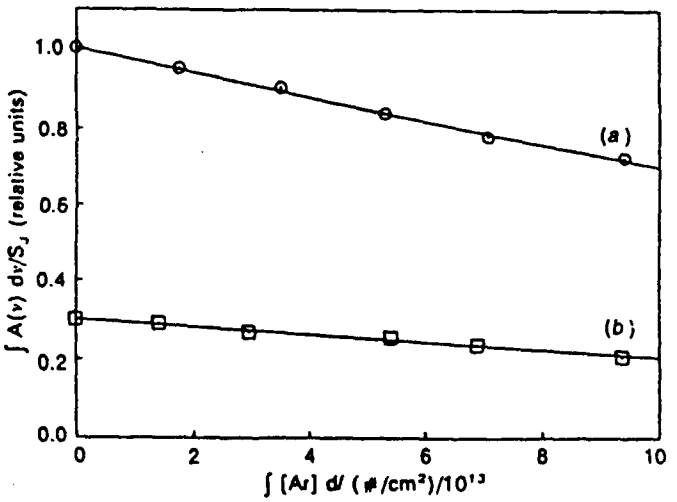

Figure 3

scattering rare gas. Note the factor of 3 difference in the initial populations due to the 3:1 nuclear spin statistics in H_2O.

2) State-resolved scattering and IR laser Dopplerimetry in open shell (Cl + HCl) collisions

As a recent thrust with the flash kinetic spectrometer, we have been investigating energy transfer in "hot atom" open shell collisions. We have completed a study on Cl + HCl, monitoring the HCl (v=1-0) transition on a series of R branch transitions up to J = 12. The Cl atoms are

prepared by excimer laser photolysis of Cl_2 molecules at 308 nm, which in principle generates a narrow Cl atom velocity distribution centered at 2000 m/s. If one includes the relative motion of the initial Cl_2 and HCl species, this translates into a center of mass collision energy for Cl + HCl of 3500 cm^{-1}, sufficient to surmount the 3000 cm^{-1} activation barrier to Cl-H-Cl, H atom exchange. The tunable F-center laser is used to probe i) the final HCl rotational quantum states and ii) the final HCl(J) velocity distributions. Although the reactive component is still relatively small at these energies, the collisions significantly sample "frustrated" reactive attempts, and thus state resolved energy transfer can probe the entrance and exit channels to reaction.

The transient absorption method looks only at changes in population, which can result from collisional excitation into and out of a given J state. However, by exploiting the Doppler signatures of the transient signals, specifically that the molecules are initially at 300 K but moving much faster after the collision, we can extract the loss and gain cross sections independently (Fig. 4).

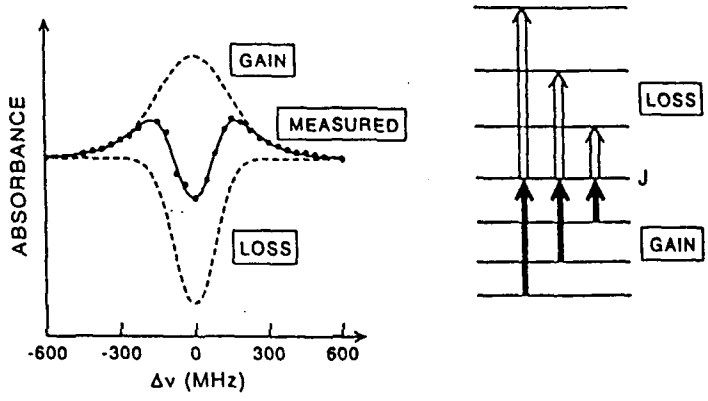

Figure 4

Furthermore, since we measure absolute absorbances, we can determine the absolute magnitude of these integral cross sections. We have used quasiclassical trajectory calculations to test the Cl-H-Cl potential energy surface of Schatz and Gordon, by comparing state-resolved inelastic cross sections with experiment. The theoretical results, shown in Fig. 5, indicate remarkably good agreement with experiment, both in J dependent trend and absolute magnitude.

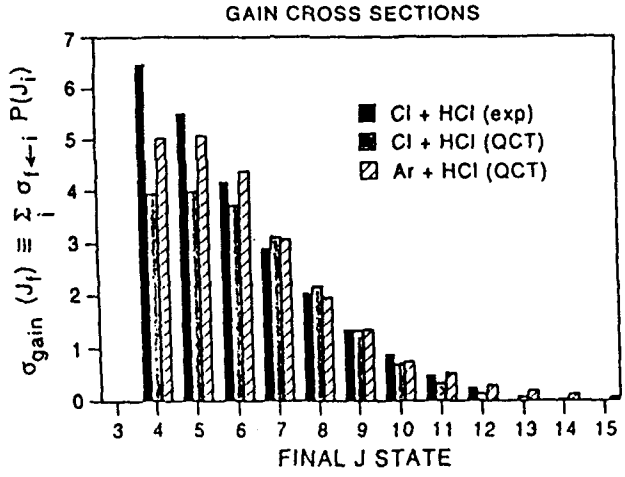

Figure 5

The maximum J" excited is 12, far from J=18 accessible at these center of mass collision energies. We find the inefficiency of this hot atom energy transfer process is not due to angular momentum constraints, but instead is a reflection of the potential surface and "heavy-light-heavy" collision dynamics. In essence, the near spherical shape of the Gordon-Schatz potential surface directs the collisional forces toward the light H atom, which can not effectively slow the Cl atom in the Cl-HCl center of mass frame.

Such a heavy-light-heavy collision model would predict strongly forward scattering of the Cl atom, which we have investigated via time resolved Dopplerimetry on the recoiling HCl quantum states. To implement these ideas, we have employed singular variable decomposition/ Green's function methods for analyzing the Doppler profiles in the single collision regime, and thereby extracting absolute state-to-state differential cross sections into a given final HCl J state. The results are shown in Fig. 6, and clearly demonstrate the anticipated trend toward strongly forward scattered HCl species. Also indicated (in solid lines) are the predictions for $d\sigma/d\Omega$ from trajectory analysis on the Schatz/Gordon surface, which again demonstrate quite good qualitative agreement with the experimental data.

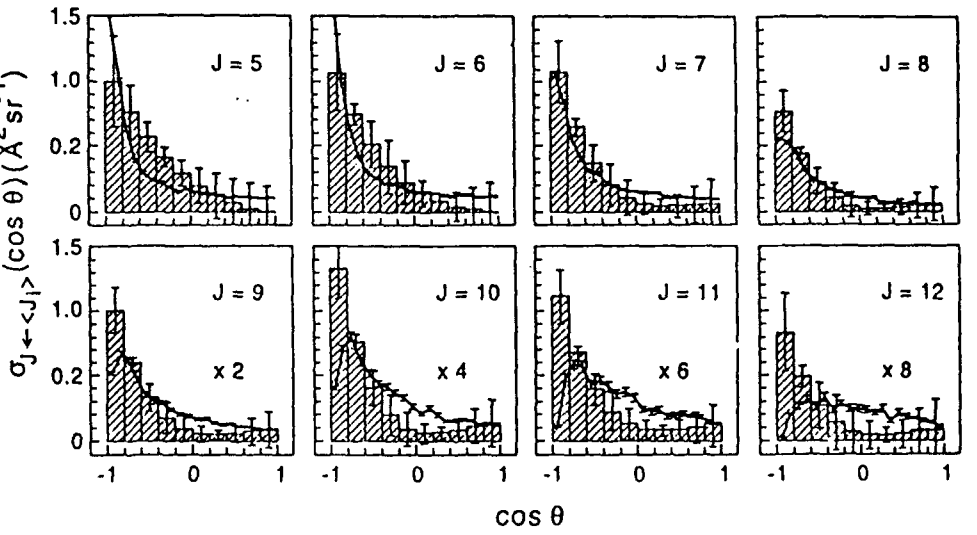

Figure 6

Publications during the 8/93 - 7/94 grant period:

1) "Pressure broadening and collisional narrowing in OH(v=1-0) rovibrational transitions with Ar, He, O_2 and N_2," A. Schiffman and D. J. Nesbitt, J. Chem. Phys. 100, 2677 (1994).

2) "Collisional alignment of CO_2 rotational angular momemtum states in a supersonic expansion," M. J. Weida and D. J. Nesbitt, J. Chem. Phys. 100, 6372 (1994).

3) "Probing potential energy surfaces via high resolution IR laser spectroscopy," D. J. Nesbitt, Faraday Disc 97, xxx (1994, in press).