STATE-TO-STATE DYNAMICS OF MOLECULAR ENERGY TRANSFER

Annual Performance Report
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During this budget period we have focussed our efforts toward completing experimental measurements of differential cross sections for fully-resolved state-to-state angular momentum transfer in NO + Ar collisions, including both the electronically adiabatic and nonadiabatic channels represented by:

We have also begun measurements of integral cross sections as a function of collision energy for state-resolved rotational excitation of the first triatomic molecule to be examined by this technique, in the system SO₂ + He.

In the NO + Ar experiments, we have addressed two specific issues: (1) extending our previous measurements¹ to much higher kinetic energies, to make possible a direct comparison of our results to those acquired by Houston and coworkers *via* an imaging technique,² and (2) the polarization of the angle-resolved and state-selected NO products, which can arise either by preferential molecular alignment or by preferential population of different Λ -doublet levels.

The first task was relatively simple to accomplish; by seeding the NO target molecule in He to increase its laboratory speed, a c.m. kinetic energy of 1694 cm⁻¹ was obtained, which can be compared with the collision energies of 117 cm⁻¹, 149 cm⁻¹ and 442 cm⁻¹ of the previous experiments. The angular distribution of the final state $j' = 18.5$ was measured for c.m.

angles between 30° and 120° . This particular final state was selected because it showed a characteristic double-rainbow structure in the deconvoluted images of Houston et al. Our results, obtained with higher resolution in both kinetic energy and scattering angle, showed structure similar to that seen by the Cornell group. This confirms both their general conclusions and the deconvolution method which they used to extract differential cross sections from the projected scattering images.

The second issue has proven more difficult to resolve. From measurements taken on the same product rotational state, but employing different spectroscopic branches for LIF detection, it is evident that there is some preferential population of different Λ -doublet levels of the products. The $R_{11}+Q_{21}$ branch corresponds to e levels, and the R_{21} and $Q_{11}+P_{21}$ branches correspond to f levels. However, it is also possible that molecules selected for both rotational state and scattering angle are preferentially aligned by collision. The probe laser in these experiments was polarized in the plane of collision. For high rotational states, lines dominated by Q branches have greater intensity for a transition dipole aligned parallel to j' , whereas P and R branches favor a transition dipole perpendicular to both j' and the internuclear axis. So far, attempts to separate these effects experimentally have yielded inconclusive results. We are still working on this problem.

On a more positive note, comparison of the experimental differential cross sections at the lower collision energies can now be made with the new theoretical results of Alexander,³ who carried out quantum close-coupling dynamics calculations on potential energy surfaces (both A' and A'' symmetry) newly calculated by the correlated-electron-pair approximation.

Unlike previous theoretical results, the new calculations of Alexander are in generally good agreement with experiment for both the final state distribution at fixed scattering angle, and the angular distribution for selected final states at fixed collision energy. Because the present calculations average over projection quantum numbers, theoretical analysis of collisional alignment effects cannot yet be carried out.

Concurrently, we have also carried out collision experiments in the system $\text{SO}_2 + \text{He}$. These are the first crossed molecular beam experiments on state-resolved rotational energy transfer of a triatomic molecule. State-to-state integral cross sections have been measured as a function of final rotational state at a fixed collision energy of 473 cm^{-1} , and as a function of collision energy for six selected final rotational states. Initial SO_2 rotational temperatures less than 3K were achieved with 0.3 mole-% of the molecule seeded in 20 atm of He. State-selective detection of the scattered products was done by LIF on the strong $\text{C}(122) \leftarrow \text{X}(000)$ transition at 445 nm, which has been analyzed by Yamanouchi et al.⁴ Because of the selection rules and nuclear spin statistics, the $k_a=0$ and $k_a=1$ subbands dominate the LIF spectrum. This data is currently being analyzed and the collision dynamics modelled theoretically for comparison. Cross sections for vibrational excitation in this system proved to be too small to measure.

¹S. D. Jons, J. E. Shirley, M. T. Vonk, C. F. Giese and W. R. Gentry, *J. Chem. Phys.* **97**, 7831 (1992); *ibid.* (full paper to be published).

²L. S. Bontuyan, A. G. Suits, P. L. Houston and B. J. Whitaker, *J. Phys. Chem.* **97**, 6342 (1993).

³M. H. Alexander, *J. Chem. Phys.* **99**, 7725 (1993).

⁴K. Yamanouchi, H. Yamada and S. Tsuchia, *J. Chem. Phys.* **88**, 4664 (1988).

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