dicated that all anion emission involved excitation of the neutral naphthols.

Time-resolved single photon counting fluorescence spectroscopy in Me_2SO enabled us to relate the steady-state observations to dynamic phenomena. In each case, the excited-state neutral lifetimes were attenuated and were within experimental error of the conjugate base rise times, indicating that deprotonation was the major source of neutral decay. Both **5CN2** and **8CN2** exhibited higher neutral decay rates than **6CN2** or **7CN2**, although the effect was not as dramatic as in the steady-state results due to the anomalously short lifetime for the 6-cyano-2-naphtholate anion.

By extending the range of excited-state acidities, cyanonaphthols provide further opportunities for proton-transfer studies in nonaqueous solvents and may provide entry into new photopolymerization catalysts. The observation that excited-state proton transfer from cyanonaphthols to Me_2SO solvent can occur without benefit of a Grotthuss chain-transfer pathway if the excited-state acidity is high enough indicates that other mechanisms of excited-state proton transfer are possible. Further studies are currently underway.

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Effect of Reactant Rotation on Hydrogen Atom Transfer

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We report gas-phase quasiclassical trajectory calculations of reaction cross sections for the transfer of a light atom between two heavier atoms on potential energy surfaces which possess a barrier to reaction. It is found that reactant rotational energy is more efficient at promoting reaction than either translation or vibration, regardless of the reaction energetics.

Investigation of the role played by each possible mode of reactant energy in enhancing the rates of elementary gas-phase exchange reactions has been an active area of research for the last three decades.[1-7] In particular, the propensity rules for comparing the relative efficacy of translation and vibration have been exhaustively investigated both experimentally and theoretically[1,2] and are summarized in the so-called "Polanyi rules".[1,2,8] The possible role of rotational energy in enhancing reaction rate has not been studied in comparable detail; indeed it is often summarily dismissed as ineffective. The most recent review of rotational effects[9] suggests that, in the most optimistic case, rotation may be comparable to translation in enhancing reaction, but that it will usually be much less effective than vibration. (However, one case[10]—a light-atom transfer—where rotation is comparable to vibration was reported.) Intuitively, it is often felt that rotational motion is "perpendicular" to the reaction coordinate and hence cannot assist in crossing the barrier to reaction. However, recent theoretical work[11,12] has clearly shown that rotational motion can couple to translation if there is significant stretching of the bond under attack. Several calculations have been published that confirm that rotation can increase reaction cross sections.[9,13-18]

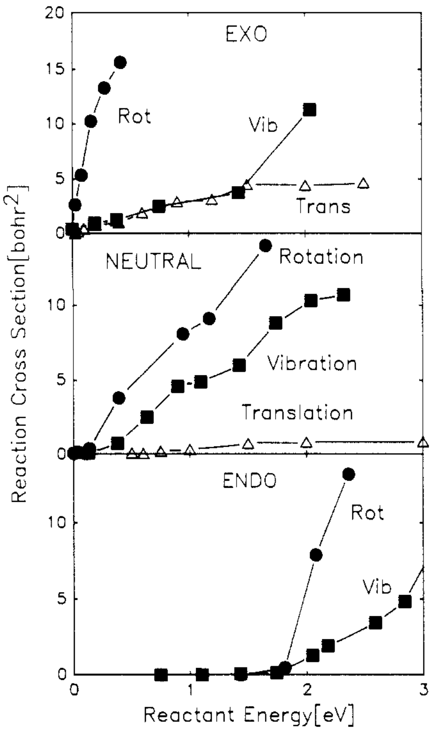

Figure 1. Reaction cross section as a function of reactant energy for the hydrogen-transfer reaction, A + HB → AH + B, on three different potential energy surfaces. Atoms A and B both have mass 19 amu; H has mass 1 amu. Note that translational energy is ineffective on the ENDO surface.

The transfer of a light atom has traditionally[19,20] served as a model for hydrogen atom transfer and (although less appropriately) for proton and hydride transfer. We have compared the relative effectiveness of reactant translational, vibrational, and rotational energy on an exoergic, and endoergic, and a thermoneutral potential surface. For our model exoergic surface we used the potential number 5 of Muckerman,[21] designed for $F + H_2$, and for our endoergic system we used the $I + H_2$ potential of Perry et al.[22] Neither of these potentials is now considered to be of chemical accuracy. However, they have the advantage of being easily programmed, are readily accessible, and have already been the subject of several trajectory studies. For the thermoneutral system we used the accurate LSTH potential[23] for $H + H_2$.

The reaction cross sections for the three systems are shown as a function of energy in Figure 1. In all cases, the zero of internal

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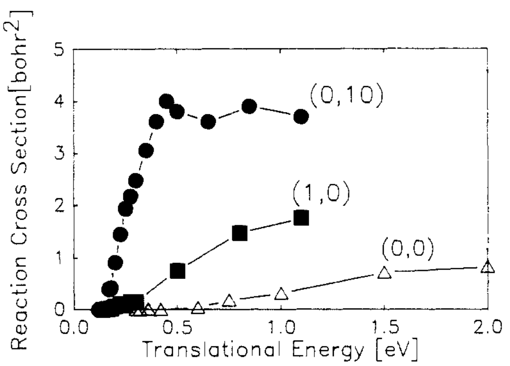

Figure 2. Reaction cross section for hydrogen atom transfer as a function of translational energy out of specific HB vibrotational states, (v,J). The potential energy surface is thermoneutral.

energy was taken as the zero-point energy of the diatomic molecule. When either rotational or vibrational energy was being varied, the collision (translational) energy was 0.5 eV (48 kJ mol^{-1}). This admittedly high energy was chosen to ensure good statistics, but the results are typical of all energies above the reaction threshold. This is illustrated by the data of Figure 2, in which the translational energy dependence of the cross section for fixed internal vibrational and rotational energy is shown.

It is clear from both Figures 1 and 2 that reactant rotation is more effective at promoting a light-atom-transfer reaction than either translation or vibration, regardless of the reaction exoergicity and the total energy. This finding is confirmed by calculations of other workers,[10,14,15] although this point is not explicitly mentioned in their papers. One apparent counterexample has been reported for O + HCl → OH + Cl by Persky and Broida.[24] On their surface II, they see a decline in reactivity with rotation. However, their rotational energy was always less than 0.5 eV. For higher rotational energy, and at higher translational energies, rotation strongly enhanced H atom transfer.[25] A recent landmark state-to-state experiment[26] which found rotational enhancement of reaction was also a light-atom-transfer reaction. Using the data of Figure 2, we can calculate[27] thermal rate constants for reaction for each case. These are $k(v{=}0,J{=}0) = 6.6 \times 10^5$, $k(1,0) = 7.4 \times 10^8$, and $k(0,10) = 1.4 \times 10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$ (±10%) at 300 K. Therefore, while vibration enhances the rate constant by 3 orders of magnitude, the same energy in rotation enhances it by more than 4. It appears that rotational excitation is the most efficient way to promote hydrogen atom abstraction.

We have, as yet, no conclusive explanation for this phenomenon. One suggestion[11] is that, as a light atom is transferred, the bond under attack stretches rapidly, strongly coupling rotational and over-the-barrier motion. Another view[10,15] is that the mass combination may allow free "figure-of-eight" motion of the H around the heavier atoms.

These results, of course, have only been shown to hold for atom + diatom reactions, and ones with a linear transition state at that. The role of rotation in reactions where the H atom is transferred between bulkier species is at present under investigation, as is the role played by the geometry of the transition state. Another caveat is that these calculations are valid only if classical mechanics gives an adequate description of the dynamics of the particles. This is the subject of current investigation. However, we believe that our data were obtained at such high total energy that the trajectory approach should predict at least the qualitative trends.

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Formation of Very Large Gold Superclusters (Clusters of Clusters) as Secondary Ions up to $(Au_{13})_{55}$ by Secondary Ion Mass Spectrometry

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Secondary ion mass spectrometry (SIMS) and plasma desorption mass spectrometry (PDMS) have been used in a systematic study to characterize different metal complexes. Both desorption techniques in combination with a time-of-flight (TOF) analyzer allow the investigation of molecular weight, fragmentation pathways, and metastability of secondary ions. Especially for ligand-stabilized metal clusters, mass spectrometry gives important information about the structure of these compounds. By means of SIMS and PDMS spectra the structure principle of the $Au_{55}(PPh_3)_{12}Cl_6$ complex is clarified to be cubic (ccp) or hexagonal (hcp) close packing.

There is an open question concerning the structure of high-nuclearity metal clusters. Two main structure types are in discussion: (1) vertex-sharing icosahedra, building upon each unit to form highly symmetric supraclusters;[1,2] and (2) cubic close packed (ccp) or hexagonal close packed (hcp) with the outer geometry of a cuboctahedron.[3] It is well-known that for smaller clusters both structures have been observed. From a theoretical point of view, the density of an icosahedral packing of atoms of the same size is lower than the density of ccp or hcp structures. Therefore it is assumed that for higher nuclear clusters icosahedral packings must sometimes collapse into the dense packed state. Up to now clusters of higher nuclearity have never been observed with an icosahedral structure.

Recently Fackler et al.[4,5] referred some peaks in the SI spectra of $Au_{55}(PPh_3)_{12}Cl_6$ to the icosahedral packing of this gold complex.[6] In this study, mass spectra were recorded with PDMS whereby broad mass distributions in the higher mass range ($m < 50000$ u) were found. The most abundant SI peaks at 8200 u, 12 800 u and 16 600 u are explained by the fragmentation of vertex-sharing supraclusters as described by Teo et al.[2] The final conclusion of this work is that Schmid's formula of this gold complex has to be corrected to $Au_{67}(PPh_3)_{14}Cl_8$.

In our experiments, measurements were carried out with a new PDMS/SIMS combination TOF mass spectrometer. This instrument can be used for comparative studies of secondary ion formation on identical samples under keV- and MeV-ion impact.[7] The instrument is described in detail elsewhere.[8,9]

The samples were dissolved in CH_2Cl_2 and dropped onto aluminum or silver foil. Negative as well as positive PDMS and SIMS spectra were taken from different sample thicknesses.[10]

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