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REACTION DYNAMICS OF ELECTRONICALLY EXCITED ALKALI ATOMS WITH SIMPLER MOLECULES

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ABSTRACT: The reactions of electronically excited sodium atoms with simple molecules have been studied in crossed molecular beams experiments. Electronically excited Na($3^2P_{3/2}$, $4^2D_{5/2}$, and $5^2S_{1/2}$) were produced by optical pumping using single frequency dye lasers. The effects of the symmetry, and the orientation and alignment of the excited orbital on the chemical reactivity, and detailed information on the reaction dynamics were derived from measurements of the product angular and velocity distributions.

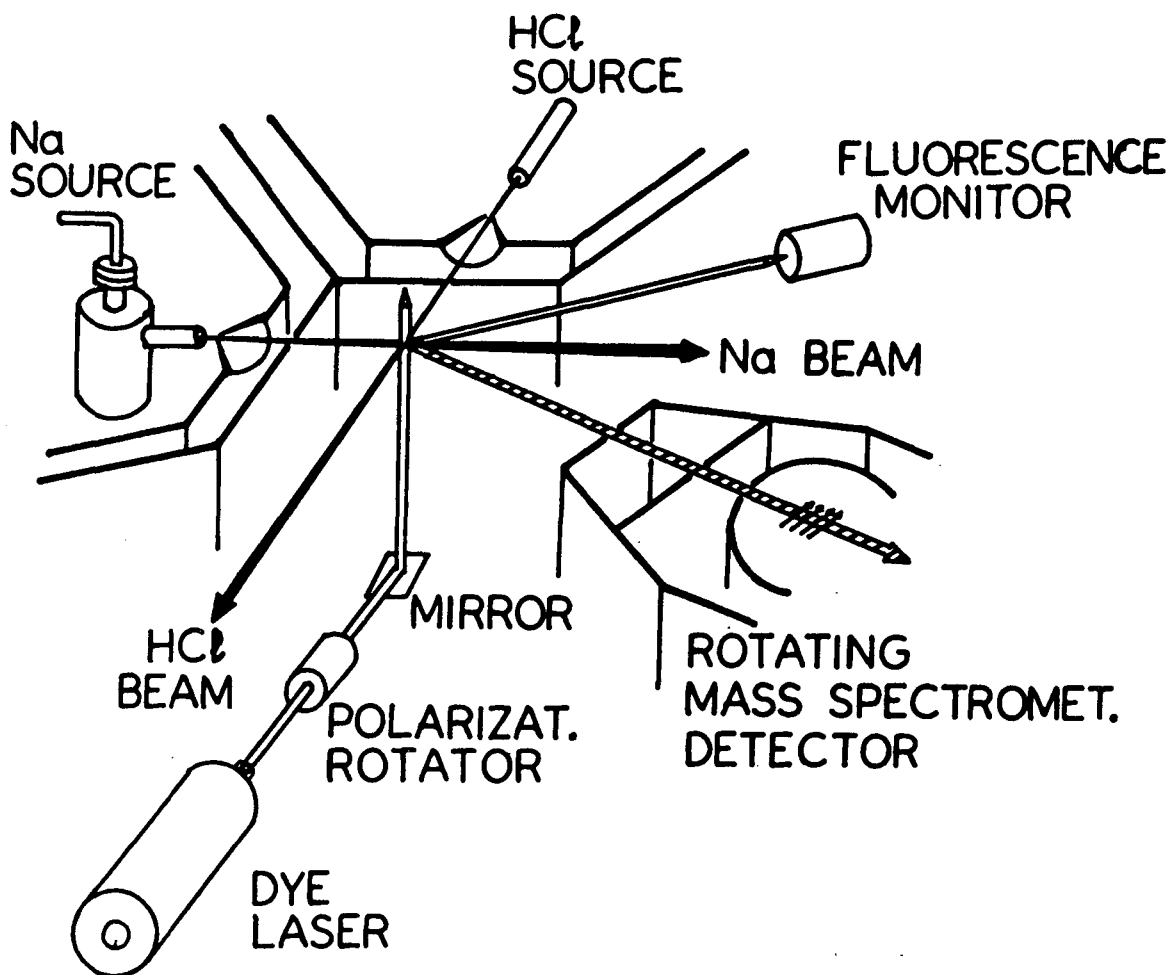
INTRODUCTION

The effects of electronic excitations of reactant atoms on reactive scattering are often quite dramatic. The large excitation energies associated with electronic transitions are often more than enough to satisfy the energy requirements of substantially endothermic reactions. But, the most important aspect of electronic excitation is the drastically different chemical behavior due to the change in the spin state or the orbital symmetry of the excited atoms. For example, in the reaction of a ground state $O(^3P)$ with a hydrogen molecule or saturated hydrocarbons, the abstraction of a hydrogen atom by an oxygen atom is the only reaction channel. On the other hand, in the reaction of electronically excited $O(^1D)$, the insertion of an oxygen atom into H-H or C-H bonds becomes the main initial step.¹ Similar behavior was also observed in the reaction of electronically excited $Mg(^1P_1)$ with hydrogen molecules.²

Recent advances in the tunable dye laser have had a profound impact on the investigation of the reaction dynamics of electronically excited atoms. Not only has it made the experimental studies of short lived excited states possible through optical excitation, but it has also allowed the investigation of the effect of the alignment and the orientation of the excited orbitals. Many such experiments have been carried out on chemiluminescent reactions of calcium atoms with small halogen containing molecules³ and on electronic to vibrational energy transfer involving alkali atoms.⁴ Some aspects of the scattering of electronically excited alkali atoms will be discussed during this conference by several participants.^{5,6} I will focus my attention on some of the very interesting results obtained from our crossed molecular beams experiments. Information on the detailed dynamics of reactions of sodium atoms excited to 3P, 4D, and 5S states with simple halogen or oxygen containing molecules is derived from the measurements of product angular and velocity distributions. The alignment and orientation dependence of the Na atoms have also been investigated.

EXPERIMENTAL

The experimental arrangement is shown schematically in Fig. 1. Two supersonic beams are crossed under single collision conditions at right angles in a liquid nitrogen cooled scattering chamber maintained at 10^{-7}



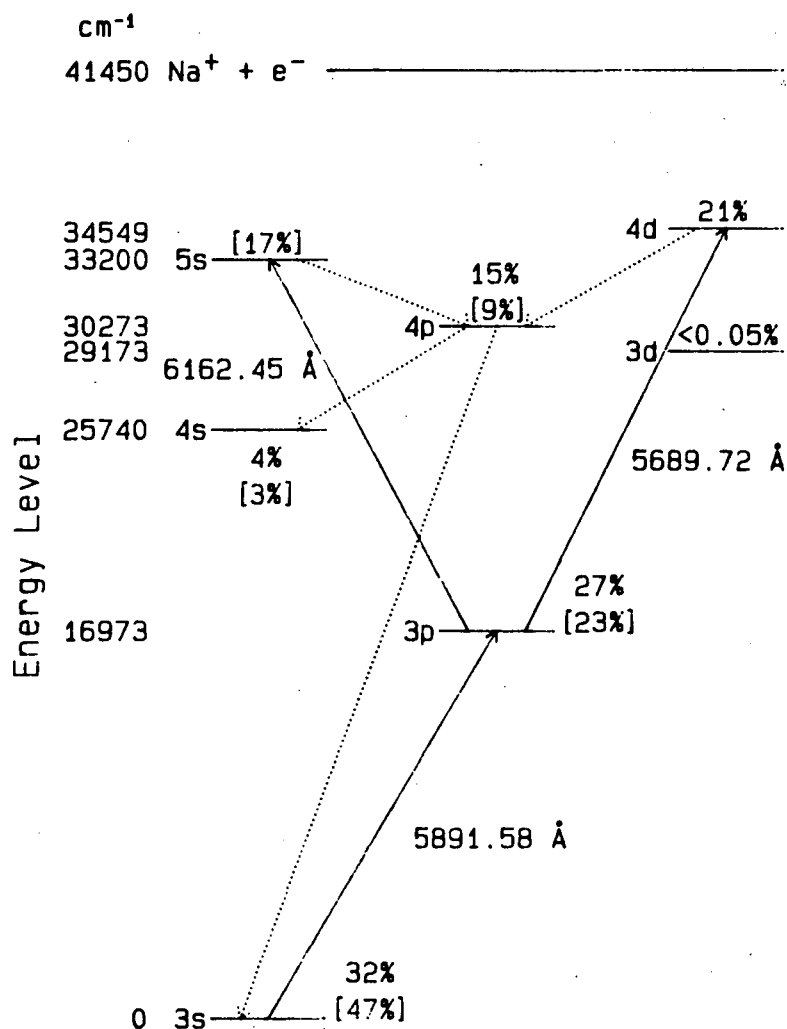
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Fig. 1. Schematic of the crossed molecular beams machine used in these experiments.

torr. Scattered product is detected with a mass spectrometer which can rotate in the plane defined by the two reactant beams. The mass spectrometer is housed in a rotatable, triply differentially pumped ultra-high vacuum detector chamber which contains an electron bombardment ionizer quadrupole mass filter, and a scintillation ion counter.

The sodium atom beam is produced by a rare gas seeded supersonic expansion from a two chamber stainless steel oven with a 100 micron diameter nozzle. The central portion of the Na beam is skimmed by a single piece, heated, stainless steel skimmer with a 1.1 mm diameter. The dimensions of the sodium beam at the collision center are determined by a

rectangular aperture to be 1 mm tall by 3 mm wide. The angular divergence of the Na beam is 1° . The creation of a large stationary fraction of $\text{Na}(3^2P_{3/2})$, $\text{Na}(5^2S_{1/2})$ and $\text{Na}(4^2D_{5/2})$ atoms by optical pumping has been adopted from the experimental techniques developed by Hertel and coworkers.⁷ The $\text{Na}(3^2P_{3/2}, F=3 \rightarrow 3^2S_{1/2}, F=2)$ hyperfine transition of the Na D_2 line (589 nm) was optically pumped using a cw single frequency dye laser locked to the peak of the sodium fluorescence in the interaction region. For exciting sodium atoms to a higher excited state, another single frequency cw dye laser was locked either to the green (569 nm) $\text{Na}(4^2D_{5/2}, F=4 \rightarrow 3^2P_{3/2}, F=3)$ transition or to the red (616 nm) $\text{Na}(5^2S_{1/2}, F=2 \rightarrow 3^2P_{3/2}, F=3)$ transition. Figure 2 shows the optical pumping scheme and the approximate relative populations of the appropriate sodium levels when these transitions are



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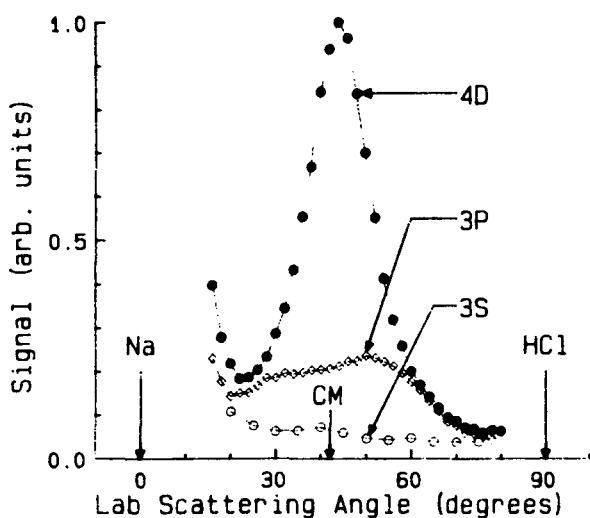
Fig. 2. Na atomic energy levels, and the approximate steady state population attained in each state when the $\text{Na}(4D)$ [$\text{Na}(5S)$] is optically pumped.

saturated. Radiative transitions led to a significant steady state population in the $\text{Na}(4^2\text{S})$ and $\text{Na}(4^2\text{P})$ levels when either the $\text{Na}(4^2\text{D})$ or the $\text{Na}(5^2\text{S})$ levels were optically pumped. The sodium velocity distribution is measured by monitoring the doppler shifted fluorescence from the 45° laser crossing, and scanning the laser frequency. The full width at half maximum velocity spread is typically 20 percent. Alignment of excited 3p or 4d orbitals can be accomplished using linearly polarized lasers for the optical pumping of these states. The orbital alignment was varied by rotating the linearly polarized lasers in the scattering plane. Orbital orientation can be effected by using right or left circularly polarized light for the excitation.

The HCl beam was formed from a heated stainless steel tube with an interchangeable nozzle affixed on the end. The temperature of the 70 micron diameter platinum nozzle was actively stabilized at 180°C to prevent HCl cluster formation. Typically, a 350 torr HCl nozzle backing pressure was used. The HCl beam is defined to have a 3 mm by 3 mm cross sectional area in the scattering region with an angular divergence of 3° . The O_2 beam and other molecular beams are operated in a similar fashion, seeded supersonic beams are produced either by premixing the reactants with rare gas or bubbling rare gas through a liquid reactant maintained at constant temperature.

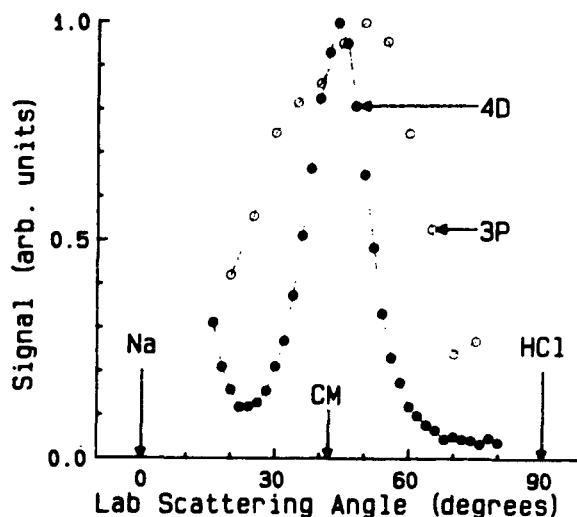
RESULTS AND ANALYSIS

The reaction of the ground state Na atoms with HCl is endothermic by 5.6 kcal/mole. Figure 3 shows the product NaCl angular distributions for $\text{Na}(3\text{S}, 3\text{P}, 4\text{D})$ at an average collision energy of 5 kcal/mole. These angular distributions were measured at a mass/charge ratio of 23 as most of the NaCl fragments yield to Na^+ in the electron bombardment ionizer, and the rising signal at low angles is due to elastically scattered Na atoms. The reactive cross section increases with increasing electronic energy. At the collision energy shown the $\text{Na}(3\text{S})$ ground state atoms react only because the high velocity components of each beam barely overcome the endothermicity of the reaction. For the reaction of the $\text{Na}(3\text{P})$ atoms, NaCl product is observed over the full laboratory angular range possible conserving momentum and the total energy of the system. This implies a broad range of product translational energies, which is borne out by



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Fig. 3. NaCl product angular distributions for the reaction $\text{Na}(3\text{S},3\text{P},4\text{D}) + \text{HCl}$ at a collision energy of 5 kcal/mole.

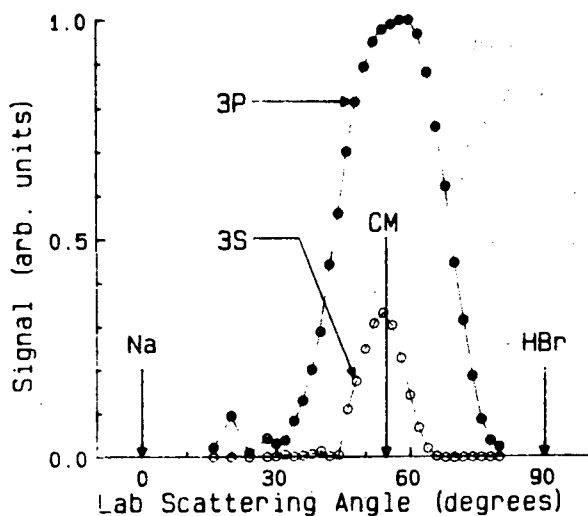


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Fig. 4. NaCl product angular distributions for $\text{Na}(3\text{P},4\text{D}) + \text{HCl}$ scaled to the same point to show the narrowing of the angular distribution at higher electronic excitation.

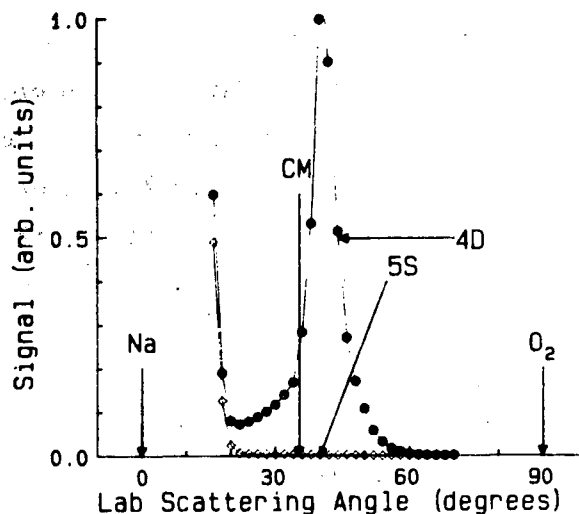
product velocity measurements. The same is not true of the reaction of the $\text{Na}(4\text{D})$ and $\text{Na}(5\text{S})$ states, in which the NaCl is scattered over a narrower angular range than that produced from the $\text{Na}(3\text{P})$ state, and thus carries less translational energy despite an extra 2 eV of excess energy. This is illustrated in Fig. 4 in which the $\text{Na}(3\text{P})$ and $\text{Na}(4\text{D})$ angular distributions from Fig. 3 have been redrawn scaled to the same level. In addition, orbital alignment studies have shown that the preferred $\text{Na}(4\text{d})$ orbital alignment for reaction has the d_{z^2} orbital pointed along the relative velocity vector of the system for any laboratory detector angle for which NaCl is observed.

The reaction of the $\text{Na}(3\text{S},3\text{P})$ states with HBr has been studied at collision energies of 3, 5, 20 kcal/mole. The ground state reaction is endothermic by 0.5 kcal/mole. The results are analogous to those for the $\text{Na}(3\text{S},3\text{P})$ reaction with HCl . There is reaction for the ground state since the collision energies easily overcome the slight endothermicity, but the cross section increases greatly for the $\text{Na}(3\text{P})$ state, as shown in the NaBr product angular distribution in Fig. 5.



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Fig. 5. NaBr product angular distributions for the reaction $\text{Na}(3\text{S},3\text{P}) + \text{HBr}$ at a collision energy of 5 kcal/mole.



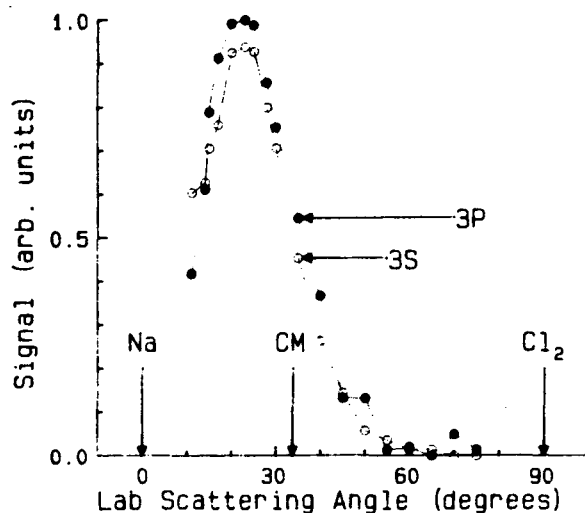
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Fig. 6. NaO product angular distributions for the reaction $\text{Na}(5\text{S},4\text{D}) + \text{O}_2$ at a collision energy of 18 kcal/mole. The rising signal at low angle is due to elastically scattered Na atoms.

The reaction of Na with O_2 to form NaO and O is particularly interesting in that there can be no ground state reaction with its endothermicity of 56 kcal/mole. Also, NaO_2 has been observed experimentally⁸ and has been estimated to be 37 kcal/mole more stable than the ground state reactants.⁹ This reaction has been studied at collision energies of 7, 16, and 18 kcal/mole. Reaction is only observed for the Na(4D) state and only at the two higher collision energies. The NaO product angular distributions for the scattering of the Na(4D) and Na(5S) states are shown in Fig. 6. Once again a mass/charge ratio of 23 was monitored as NaO fragmented in our ionizer to give Na^+ . The fact that no reaction product is observed for Na(5S) implies that the Na(3S,3P,4S,4P) states all do not lead to NaO product, as each of these states is produced in the optical pumping of the Na(5S) state as illustrated in Fig. 2 above. Another remarkable feature of this reaction is that the NaO product is scattered backwards in the center of mass frame of reference with respect to incoming Na atoms (i.e. to larger laboratory

angles than the center of mass angle of the system). This implies a direct reaction with no collision complex formation, and a collinear approach geometry. This is even more interesting in that the NaO product translational energy is very small compared to the total energy available for translational -- over 2 eV goes into the internal degrees of freedom of the products. Thus it is possible that only $O(^1D)$ atoms are being produced in this reaction. Polarization dependences show a marked dependence of the preferred orbital alignment for reaction on the laboratory detector angle.

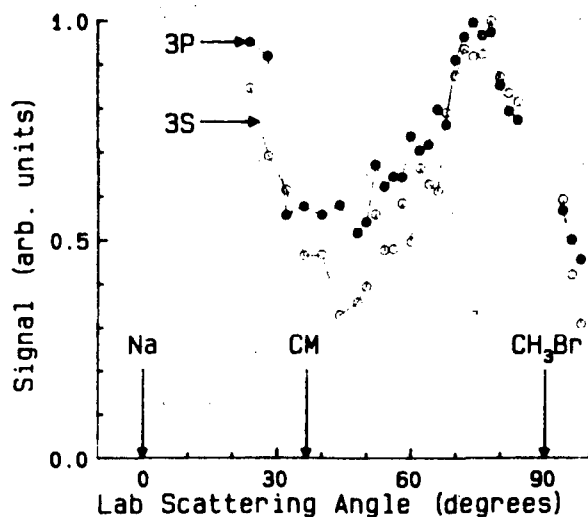
The reaction of Na with Cl_2 is a classic harpoon type reaction in which an electron transfers at long range from the Na to the Cl_2 , and then "reels in" the Cl^- from Cl_2^- . The production of NaCl and Cl from ground state reactants is exothermic by 39.4 kcal/mole. At collision energies of 3, 5, and 19 kcal/mole, no large difference was observed in the product angular distributions of the Na(3S) and Na(3P) states as shown in Fig. 7, even though the electronic excitation effectively lowers the ionization potential of Na by over 2 eV.



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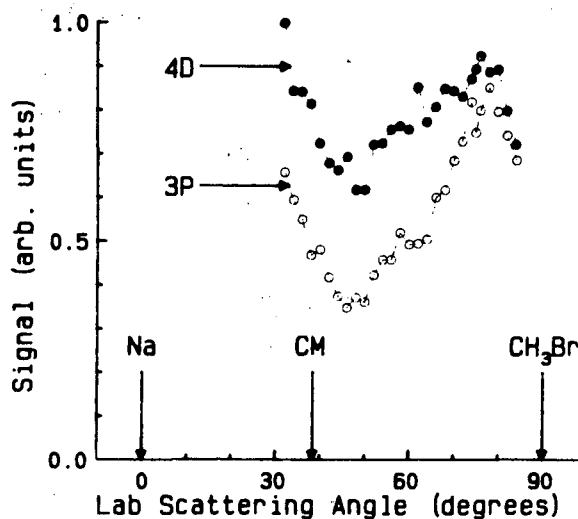
Fig. 7. NaCl product angular distributions measured for the reaction $Na(3S,3P) + Cl_2$ at a collision energy of 19 kcal/mole.

The reaction of Na with CH_3Br is a typical example of the well studied alkali + methyl halide family.¹⁰ It is a classic rebound mechanism reaction with a ground state exothermicity of 16.7 kcal/mole. This reaction was studied at collision energies of 21 and 24 kcal/mole. Figure 8 shows a NaBr product angular distribution at a collision energy of 21 kcal/mole. The broad back scattered peak arises from the "steric factor," that is, the Na must approach the Br end of the CH_3Br , and bounces back as a NaBr. If the Na approaches the wrong end of the CH_3Br , there is no chance of reaction. The higher signal for the higher



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Fig. 8. NaBr product angular distributions measured for the reaction $\text{Na}(3\text{S},3\text{P}) + \text{CH}_3\text{Br}$ at a collision energy of 21 kcal/mole.



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Fig. 9. NaBr product angular distributions measured for the reaction $\text{Na}(3\text{P},4\text{D}) + \text{CH}_3\text{Br}$ at a collision energy of 21 kcal/mole.

excited states at the low angle side of this back scattered peak is due to a relaxing of this steric factor, and an opening up of the angle of acceptance for chemical reaction with increasing Na orbital size. The statistics were insufficient for the measurement of polarization dependences for this system, but these would certainly be of great interest.

DISCUSSION

The most interesting results of the $\text{Na} + \text{HCl}$ reaction are the drastically different translational energy release between the reaction of $\text{Na}(3\text{P})$ and $\text{Na}(4\text{D})$. These can be explained with a simple electron transfer picture and the repulsive interaction between H atom and NaCl products. HCl is known to be dissociated by slow electrons, and has a negative vertical electron affinity of approximately 1 eV. For the reaction of the $\text{Na}(3\text{P})$ atoms this electron transfer becomes energetically possible at 3.5 Å. This is incidentally the peak of the $\text{Na}(3\text{P})$ orbital density. What the departing H atom feels is the repulsion of the Cl atom of the fully

developed closed shell NaCl molecule, and a significant impulse can be given to it. In the case of the Na(4D) atoms, the crossing of the neutral and ionic potential curves (the initial point of electron transfer) moves out to 7.7 Å. Thus, an electron transfers over, HCl⁻ dissociates, the H atom departs and the Na⁺ and Cl⁻ are drawn together. There is nowhere for the highly vibrationally excited NaCl to dump any of its energy as the H atom is already gone. The H atom has only felt the repulsion of the loosely bound or highly vibrational excited NaCl. This interpretation is borne out by the polarization measurements in which the favored alignment of the Na(4d) orbital for reactive signal at any laboratory detector angle is along the relative velocity vector of the system. This corresponds to pointing the 4d orbital towards the HCl, because at long range the relative velocity vector in the laboratory is the direction from the Na to the HCl. The observed difference in the translational energy distributions of products from Na(3P) and Na(4D) also suggests that the DIPR-DIP model,^{11,12} in which products are expected to be distributed as in photodissociation, does not provide a good description of these reactions. The repulsion between H and NaCl as a whole needs to be considered rather than just between H and Cl⁻.

The results of the state selective Na + O₂ reaction must be explained on the basis of the symmetry of the reactant and intermediate states. A very likely event in an encounter between an Na atom and an O₂ molecule is electron transfer leading to stable collision complexes with C_{2v} symmetry. These complexes can be more stable than ground state reactants.¹¹ While these complexes are certainly formed in our experiment, they apparently do not lead to the production of NaO. The fact that all of the NaO produced was back scattered with respect to the incoming Na atoms in the center of mass frame of reference implies a Na-O-O collinear approach geometry, and a direct reaction -- no collision complex formation. Complexes that are formed would most likely decay via the lowest energy pathway open to them -- quenching to Na(3S) + O₂(X³Σ_g⁻, a¹Δ). Since only the Na(4D) state reacts to form NaO it must at least partially avoid triangular Na⁺O₂⁻ complex formation in the entrance channel. Our detector is not state selective, so that we can only use conservation of energy and thermochemical arguments to determine product states. The narrow product angular range suggests the possibility of the formation of O(¹D) atoms. The only C_{∞v} states accessible to the Na(4D) state and not to Na(nS, nP) states are NaO₂(Δ) states, so it is assumed that the intermediate is

of Δ symmetry. This is consistent with the production of $O(^1D)$ atoms although ground state products could also be generated from such a state. Polarization dependences show a steadily varying favored angle with center of mass scattering angle. The most backwards scattered product shows a favored alignment of the $Na(4d)$ orbital perpendicular to the relative velocity vector. This is consistent with the avoidance of electron transfer in the entrance channel.

The $Na + Cl_2$ reaction shows little or no effect with electronic excitation, even though the outermost point for electron transfer has moved from 5.2 Å to 22.3 Å in optically pumping the $Na(3P)$ state. With a neutral-ionic curve crossing at 5.2 Å, a significant portion of the ground state atoms are slipping through without reacting to form $NaCl$. Electron transfer becomes inefficient at larger interatomic distances, and when the crossing point is moved out even farther, it has little effect on the reaction.

The reaction of $Na + CH_3Br$ can be simply explained as mentioned above by a rebound mechanism that has been sufficient to describe all the alkali + methyl halide reactions so far studied.¹⁰ The opening up of the angle of acceptance with higher Na excited states is seen as an opening up of the center of mass scattering angle, evidenced by the increase in signal at the forward (low angle) side of the back scattered peak.

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