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Observation of structure in transition state spectra of the bimolecular reactions $K + XNa \rightarrow KX + Na$ ($X = Br, Cl$)

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Experimental studies of chemical reaction dynamics usually attempt to draw inferences about the reaction process by monitoring the product states formed from reactant states prepared as specifically as possible. Recently, several experimental techniques have been developed¹ to observe directly the spectra of species in the process of chemical reaction. The early studies² in this field focused primarily on establishing the possibility of making experimental observations of such "transition region species" (TRS). Little new insight was obtained into the reaction event, largely because the spectra were essentially featureless. It was widely believed that featureless spectra would always result for bimolecular reactions because it seemed impossible to avoid averaging over a wide range of impact parameters.

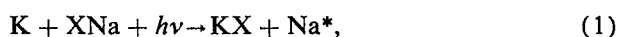
Photodissociation or "half-collision" experiments avoid such averaging by preparing a dissociative state in a known geometry. The beautiful experiments of Kinsey,³ Neumark,⁴ and Zewail⁵ have produced specific information which can be interpreted in terms of the dynamics of the dissociation process. In a nice extension of these photodissociation experiments, Bernstein and Zewail⁶ have observed the time evolution of OH formed by reacting CO₂ with H atoms prepared by Wittig's technique⁷ of photodissociating the van der Waals molecule, HI \cdots CO₂. This latter approach has the significant advantage of reducing the averaging over the impact parameter but this advantage is obtained at the expense of constraining the geometry of the reaction system in ways which may not be representative of free space reactions.

Because most chemical reactions involve a full collision with its attendant range of impact parameters, it seems important to develop experiments which probe full bimolecular reaction processes. Therefore, we have continued studies of transition region species formed in bimolecular collisions, in spite of their inherent limitations, in hopes of obtaining some insights into the reactive collision which might enlarge and complement that obtained in the photodissociation experiments. We report here spectra for the KClNa and KBrNa bimolecular transient systems. We find that the spectra of the TRS obtained are not featureless: clear structure is observed in the TRS spectrum in the bromide case.

The reactions studied are $K + XNa \rightarrow [KXNa]^{\ddagger} \rightarrow KX + Na$. In the experiment, the transition region species, $[KXNa]^{\ddagger}$, are continuously produced in

crossed beams of K and NaX. A tiny fraction of the TRS's are electronically excited by a cw dye laser to $[KXNa]^{\ddagger*}$. This species decomposes to give either $KX + Na^*$ or $K^* + XNa$. Decay into the electronically excited reactive channel is monitored by measuring the intensity of the Na^{*} emission at 589 nm.

The apparatus is similar to that previously described,⁸ with several changes which have improved the stability and run-to-run reproducibility. Quasieffusive beams of K and NaX ($X = Cl$ or Br) were crossed inside the extended cavity of a cw dye laser where the circulating power density was estimated to be ≈ 3 kW/cm². Light from the crossing region was collimated by an f/1.5 achromat, passed through an interference filter with a bandwidth of 0.3 nm centered at 589.0 nm (passing only one Na D line), and pulse counted with a cooled C31034 PMT. Excitation by dye fluorescence of Na atoms present as impurities in both beams is eliminated by placing a Na heat pipe oven inside the cavity. Each of the 3 beams was separately flagged and data was acquired in all 8 beam-on, beam-off combinations. The "3-beam" signal (3BS) is the signal with all three beams on after contributions from processes involving all 0, 1, and 2 beam signals are subtracted. The 3BS can be thought of as a three-body process



and the "3-beam" signals are normalized by dividing by each beam intensity to yield the three-body analogue of a cross section.

The excitation spectra for KXNa are shown in Fig. 1, where the normalized 3BS (Na^{*} fluorescence intensity at 589 nm) are plotted vs the excitation laser wavelength. It is immediately apparent that the spectrum for KBrNa is different from that for KClNa. Our earlier Cl spectrum appeared rather featureless, but with improved beam stability we observe a minimum near 600 nm. (The collective data⁸ suggest a broad maximum ≈ 660 nm.) For the Br case, a minimum near 600 nm is again observed, but the maximum is ≈ 608 nm and is well resolved.

In previous work on the $K + NaCl$ system a number of tests were performed to eliminate possible artifact sources of the 3-beam signal. Experiments such as magnetic (Stern-Gerlach) deflection experiments⁹ allowed us to rule out the possibility that Na^{*} arose from reactions of laser-excited K₂. We concluded from these tests that we had

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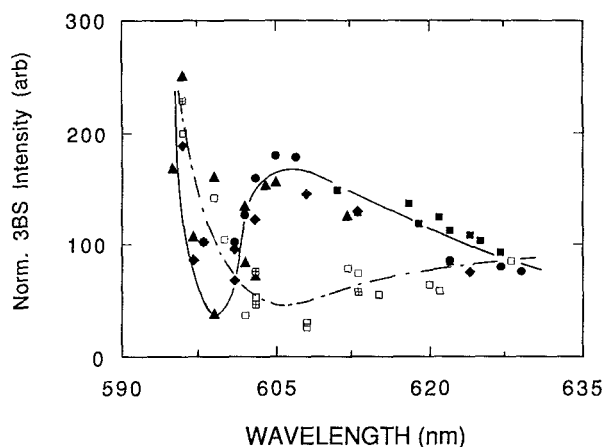


FIG. 1. Normalized 3-beam signals at the Na D line 589 nm in the NaCl + K and NaBr + K systems as a function of excitation wavelength. The dark points are bromide system signals and the open points are chloride system signals. The different point symbols correspond to data obtained on different runs. The curves are drawn only for illustration.

observed excitation of $[\text{KClNa}]^{\ddagger}$. In going from the chloride to the bromide system, nothing is changed except the salt beam; therefore, only artifacts which might involve changes in species in the salt beam need to be considered. There is no salt beam photoluminescence at the Na D line for either system. The concentration of Na atoms in the NaBr beam is observed by using direct excitation to be less than that in the NaCl beam. It was verified that the 3-beam signal in K + NaBr is from Na^* (as had already been established for K + NaCl) by tilting the interference filter which changes the wavelength transmitted. We therefore believe that the Br spectrum in Fig. 1 is that of $[\text{KBrNa}]^{\ddagger}$. Experiments were run alternating the salts and the spectra were found to be reproducible. The Br and Cl signals shown in Fig. 1 are obtained under similar conditions¹⁰ permitting meaningful comparison of the signals from the two systems.

The cross-sections for the dark reactions, $\text{K} + \text{XNa} \rightarrow \text{KX} + \text{Na}$, are large with reaction occurring on every gas kinetic collision without activation barriers. Thus the systems move quite freely on the $1^2A'$ ground state potential energy surface (pes) exploring a wide range of configurations in the reaction process. The laser field can induce transitions to excited pes's. There are two low-lying excited surfaces, the $2^2A'$, and $3^2A'$, but it is believed that only the $3^2A'$ is accessible at the wavelengths used here (600–700 nm). In the Born–Oppenheimer, stationary phase approximation, for a given instantaneous nuclear configuration $\{r_i\}$, the reacting system can absorb a photon only if the laser is tuned very near the frequency, $\nu = h^{-1}(V_3\{r_i\} - V_1\{r_i\})$. Equivalently, for a given laser frequency, systems will be excited only if they pass through nuclear configurations $\{r_i\}$ on the $1^2A'$ pes which are resonant with the laser. Once excited to the $3^2A'$ surface, the system can evolve to either K^* or Na^* . The latter (reactive) process is observed by monitoring fluorescence from the Na^* .

The structure shown in Fig. 1 has survived in spite of

averaging over thermal distributions, orientations, and impact parameters and clearly differs for the two chemical systems. Such a spectral feature could arise from (a) a region of the pes which is traversed by a reasonable fraction of collisions where the potential energy surfaces are relatively parallel (so that many nuclear configurations can absorb at basically the same frequency) or from (b) a region of the lower potential surface where the evolving system lingers, increasing the probability of transition.¹¹

The 3-beam signal rises steeply in both systems as the laser is tuned towards the Na atom D line. This might arise from excitation of the newly formed Na atom in the exit channel while it is still perturbed by the salt molecule, but we regard this as only a tentative conclusion. These signals could also be due to collision-broadened absorption of Na atoms (impurities in both beams), although our signal estimates for this process are much smaller than the signals observed. If the rise near the D line is associated with excitation of the TRS in the exit channel, the interaction shifting the frequency from the D line center is most likely due to dipole-induced dipole or dispersion effects differing only mildly between systems. Indeed, the normalized signals are observed to differ only slightly. Such features can be classified as type (a) arising from parallel surfaces.

The maxima in the spectra (near 608 for the Br and ≈ 660 for Cl) clearly depend on the reaction and probably come from excitation in the heart of the reaction region. At present it is unclear whether they can be better characterized as representing type (a) behavior (parallel pes's) or by type (b) behavior (ground state dynamics). The $\text{M} + \text{M}'\text{X}$ exchange reactions are known to occur via collision complexes with lifetimes on the order of the rotational periods¹² and stable MXM' species have been observed experimentally¹³ and predicted theoretically.¹⁴ Trajectory calculations on ground pes's suggest¹⁵ that some trajectories become "trapped" in snarled trajectories in limited regions of the pes and excitation from these "pools" might be expected to produce maxima in the spectrum.

For the KClNa reaction, surface hopping trajectory calculations¹⁶ of the Na^* excitation spectrum have been carried out and do not predict a maximum to the red of the Na D lines, but instead show only a monotonic decline in the probability of forming Na^* as the wavelength is tuned to the red. It is not known what modifications, if any, of the pes's used in these calculations could result in the prediction of a maximum. An interesting conjecture is that the maxima observed might arise through collisional non-adiabatic transitions to the $2^2A'$ electronic surface.¹⁷ Once accessed, systems in the $2^2A'$ state would be trapped for a considerable time with a consequent increase in excitation probability.

It thus appears that the blue feature of the excitation spectrum seems understandable from simple theory, but that the origin of the red feature is as yet unknown. Observation of clear structure in the NaBr + K system brings renewed hope that these experiments will provide useful information on bimolecular systems in the process of reaction.

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