Photoexcitation of the NaKCl Reaction Complex

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Emission at the Na *D* lines has been observed from the intersection of crossed molecular beams of K and NaCl irradiated by a cw dye laser in the wavelength range 600 to 700 nm. The signal is approximately independent of wavelength in this region but decreases near 700 nm. This three-beam signal is attributed to Na* formed by photoexcitation of the NaKCl reaction complex. The effective two-body cross section is circa 10^{-21} cm^2 in a laser field of ~3000 W/cm^2.

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The processes which take place when chemical reaction occurs are of fundamental interest. Because of the short time periods ($<10^{-11}$ sec) involved, experimental probing of the reaction event has essentially been restricted to comparisons of the states of the products formed with the states of the reactants introduced.[1] Reconstructing the reaction event from such data is very difficult[2] and experimental methods for probing the reaction event directly are clearly needed. In this Letter, we report observations which we interpret as arising from absorption of a photon during the reaction between NaCl and a K atom.

We shall refer to the species (neither reactants nor products) thought to have a transient existence during the reaction event as the reaction complex. The steady-state concentration of reaction complexes is quite small[3] and excitation must be detected indirectly. Recently, several efforts have been made to develop methods for observing the absorption or emission of radiation during the event. Emission at 500 nm, induced by flash-pumped dye-laser excitation of the crossed-beam (K, $HgBr_2$) system, was observed[4] in this laboratory and attributed to emission from HgBr* formed by photoexcitation of the reaction complex, $KHgBr_2$. Polyani and coworkers[5] studied the very exoergic (Na_2, F) reaction in crossed beams and observed broad, weak emission at wavelengths near the Na *D* lines which they attributed to the reaction complex Na_2F. Trajectory calculations[6] suggest that structure in these Na *D*-line wings might be observed to provide information regarding the potential surface of the system. Other investigators (see Ref. 3) have reported related observations.

An energy diagram of the system under study is shown in Fig. 1. The dark reaction occurs on nearly every collision and forms a long-lived (many rotational periods) collision complex[7] giving a relatively high steady-state concentration of complexes. The reaction exoergicity,[8] 1750 ± 1050 cm^{-1}, is insufficient to form excited electronic states of any reagent or product. If the reaction complex were to absorb a photon with $\lambda \lesssim 700$ nm, however, the Na* $3p(^2P_{3/2,1/2})$ states would be energetically accessible and we believe we have observed this process. No single-photon absorptions[9] of cold reagents or products are known in the wavelength range 600–700 nm.

Molecular beams of NaCl and K cross at 120° and are detected as in Ref. 4. The reaction zone (RZ) is now inside the extended cavity of a Spectra-Physics model 375 cw dye laser.[10] The laser is normally tuned with a two-plate birefringent filter with a bandpass of 5.3 cm^{-1}, but some diagnostic measurements were made with a thin etalon which narrowed the bandwidth to ~1 cm^{-1}. The laser is *not* focused at the RZ, having a diameter of about 2 mm in that region. Rhodamine-6G and DCM were pumped with a CR-18 Ar^+ laser. Trace amounts of sodium (10^{-4}–10^{-5}) were present in both beams and the dye

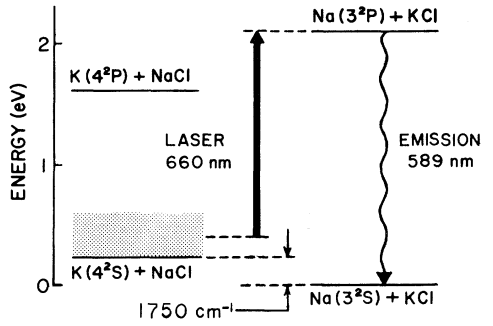

FIG. 1. Energy-level diagram for process under study. Laser is resonant with neither reactants nor products. First excited states of salts are near 30 000 cm^{-1}; shaded area corresponds to thermal energy.

fluorescence (even while lasing at significantly different frequencies) was sufficient to excite these atoms. A sodium heat pipe oven was placed in the cavity and effectively eliminated dye fluorescence at the Na D lines. Intracavity power was monitored by measuring the intensity reflected from a Brewster window on the vacuum apparatus.

Light from the RZ was collimated with a $f/1.5$ lens, passed through one or more filters, imaged and masked to reduce scattered light, and detected with a cooled (−25 °C) RCA C31034 photomultiplier. A Pomfret Research Optics Inc. model 10-5890 interference filter with a 1-nm bandwidth centered at 589 nm (passing both Na D lines) and/or an Ealing 35797 interference filter centered at 589.6 nm with a 10-nm bandwidth was normally used, but later runs were made with a filter (Pomfret) with a bandwidth of 0.47 nm full width of half maximum centered at 589.0 nm (and passing only the 589.0-nm D line).

Some light (radiation from ovens, scattered light, etc.) is emitted from the RZ and passes through the filter for various combinations of one or two beams. In order to account for these contributions to the total signal, the K beam and laser were modulated at 20 and 90 Hz, respectively, and the NaCl beam was flagged on and off.

TABLE I. Counting rates ($\pm 1\sigma$) for observation of Na D radiation with various combinations of K, NaCl, and light beams for irradiation at $\lambda = 660$ nm.

Signal	Origin	Counting rate (s^{-1})
R_{000}	Dark current	4.5 ± 2
R_{001}	Scattered light	4.4 ± 4
R_{100}	K background	-0.5 ± 3
R_{010}	NaCl background	-1.2 ± 3
R_{101}	K photoluminescence	51.3 ± 9
R_{011}	NaCl photoluminescence	23.1 ± 7
R_{110}	Chemiluminescence	1.1 ± 4
R_{111}	Three-beam signal	219.4 ± 20

A PDP 11/23 computer with a CAMAC interface operated the machine and acquired data in all eight beam on-off configurations. Gating signals from the beam choppers enabled[10] the inputs of two scalers, one to count PMT pulses, the second to count clock pulses, to determine the counting time in each configuration.

Counting rates for a given beam combination are denoted S_{ijk}, where i, j, k are 0 or 1 to indicate K, NaCl, or laser off or on, respectively. (The dark count rate is S_{000}, for example.) The elementary signal processes (Table I) involving 1, 2, or 3 beams are assumed to be additive, e.g.,

$$S_{111} = R_{111} + R_{011} + R_{101} + R_{110} + R_{001} + R_{010} + R_{100} + R_{000},$$

where R_{ijk} is the corresponding counting rate for the elementary process. The signal attributed to processes involving all three beams, the three-beam signal, is given by

$$R_{111} = S_{111} - S_{011} - S_{101} - S_{110} + S_{010} + S_{001} + S_{100} - S_{000}.$$

Typical results of 5-min counting period are shown in Table I. The signal of interest, R_{111}, (hereafter referred to as 3BS) is a combination of all signals, which accounts for the large uncertainty.

The 3BS, as shown in Table I, is positive, relatively reproducible, and persists over a very large frequency interval. Figure 2 shows the 3BS versus laser wavelength corrected for drift during a day's run and normalized for comparison between different days. Scatter is probably due to variations in one or more beam intensities. The dependence on laser power is shown in Fig. 3, and appears to be linear indicating that a single-photon process is responsible for the 3BS. Use of different Na filters separately and in combination show that the light responsible for the 3BS is centered at the Na D lines.

The existence of a 3BS only shows that all three reagents are *necessary*, and does not rule out possible sequential events such as

$$A + h\nu \rightarrow A^*, \tag{1a}$$

$$A^* + B \rightarrow \mathrm{Na}^* + ?, \tag{1b}$$

where A and B represent unknown species in each of the beams. A and/or B cannot represent either reagents (NaCl, K) or products (Na, KCl) because no single-photon absorptions are known in this region for any of these species. The possibility that impurities in the beams produce artifact signals through process 1 is difficult to rule out completely. The most obvious impurity is K_2 which is known to absorb in the red. To test the role played by K_2, the laser was etalon tuned to a local minimum in K_2 photoluminescence and thence to an adjacent K_2 bandhead at

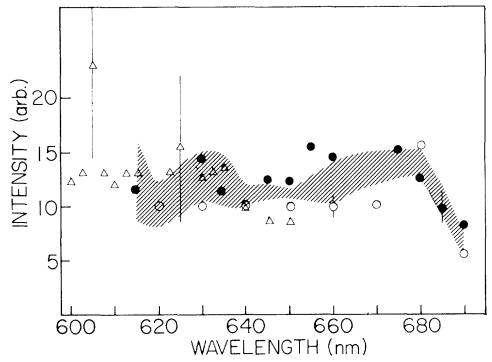

FIG. 2. Three-beam signal vs excitation wavelength. Shaded area represents smooth interpolation of the average ($\pm 1\sigma$) of two or more points at a given wavelength. The various symbols used correspond to runs on different days; representative error bars are $\pm 1\sigma$.

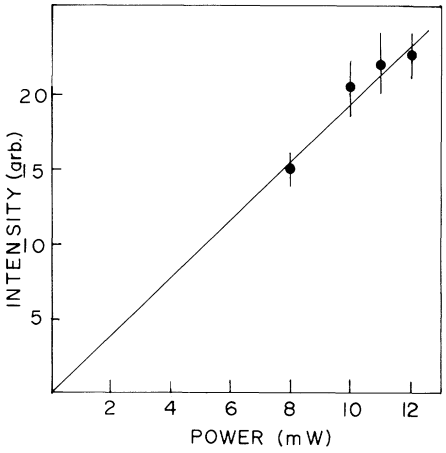

FIG. 3. Three-beam signal vs laser power.

several wavelengths near 615 nm. The photoluminescence (viewed through a Melles-Griot SWP 019 and an infrared blocking filter) varied by a *factor* of 15, but the 3BS (viewed through the Pomfret filter) varied by less than 10%. We conclude that any role played by K_2 in process (1a) can be ruled out because the 3BS is completely uncorrelated with the formation of K_2*. In addition, separate experiments using a Na beam with a NaCl or K beam show no 3BS. We are unable to think of any single-photon processes involving both reagents in which red photons can be upconverted to yellow photons at the Na D lines consistent with the experiments.

If the 3BS arises from the laser-assisted reaction

$$K + NaCl + h\nu \rightarrow Na^* + KCl, \quad (2)$$

the energetic threshold is expected at a photon energy given by

$$\epsilon_t = \epsilon_D - \epsilon_{kT} - \Delta D_0^0,$$

where ϵ_D is the energy of the Na D line, 16 970 cm^{-1}, ΔD_0^0 is the difference in bond dissociation energies, 1750 ± 1050 cm^{-1}, and ϵ_{kT} is the total available thermal energy, 2800 cm^{-1}, giving $\epsilon_t = 12\,400 \pm 1050$ cm^{-1}. This predicts that the threshold must be to the blue of 800 ± 50 nm, consistent with the apparent threshold in Fig. 2. Reaction 2 is expected to be linear in laser power, and the emission must be that of the Na atom and centered on the Na D line. We conclude that we have observed the laser-assisted reaction (2) for wavelengths in the range 600–700 nm. We roughly estimate[11] the effective two-body cross section to be 10^{-21} cm^2 in a laser field of ~3000 W/cm^2.

The laser-assisted reaction (2) is probably best viewed as an excitation of the transition state or reaction complex (denoted by $\ddagger$)[12]

$$(Na \cdot\cdot Cl \cdot\cdot K)^{\ddagger} + h\nu \rightarrow (Na \cdot\cdot Cl \cdot\cdot K)^{\ddagger *}$$

followed by decomposition of the excited state of the reaction complex

$$(Na \cdot\cdot Cl \cdot\cdot K)^{\ddagger *} \rightarrow Na^* + KCl.$$

This interpretation is inspired by the experimental observation[7] that the dark reaction proceeds through a complex persisting for several rotational periods and by pseudopotential calculations[13] for the NaKCl surface which predict a ground-state potential well ~4500 cm^{-1} deep for highly bent geometries. Classical trajectories[14] on this surface suggest that the reaction proceeds largely through triangular complexes with lifetimes of 2–3 psec.

The pseudopotential calculations also predict that the NaKCl complex has a low energy, stably bound, excited state with geometry different from the ground state. An optical transition between the ground and excited surfaces near threshold would require a large change in geometry resulting in a broad absorption band as suggested by Fig. 2. Therefore, it is tempting (but premature because of the as yet poor signal-to-noise ratio) to conclude that the complex undergoes a large geometry change during the transition. The low signal-to-noise ratio also prevents us from discerning whether the spectrum is truly featureless, or if it contains features which might be related to the time the complex spends in particular regions of the ground-state surface.[6]

The mere observation of signals at wavelengths near threshold indicates that there is no significant barrier to dissociation of the excited complex into Na* and KCl.

These experiments show that photoexcitation of the reaction complex is feasible. Although the present experiments have probed only the channel that forms Na*, several other channels are open to the excited complex. The excited complex could also decompose nonreactively to form K*, which may be the more favored route on the upper surface since a statistical breakup of the excited complex would favor the more exoergic channel. The excited complex itself might fluoresce. Dark channels are also open, and the excited complex could undergo internal conversion to yield ground-state reactants or products. So far little information is available about these other channels,[15] but work is currently underway to investigate the possibilities.

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[1]*ACS Symposium Series*, edited by P. R. Brooks and E. F. Hayes (American Chemical Society, Washington, D.C., 1977), Vol. 56.

[2]See, for example, *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1980).

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[11]K oven: boiler ~700 K, nozzle ~ 900 K; NaCl oven ~ 1300 K. Beam densities were estimated from geometry and consumption; circulating laser power was estimated to be 100 W.

[12]NaCl dimer is also present in the beam [R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956)], and we are not able to rule out the possibility that the reaction complex is $K(NaCl)_2$.

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[15]We have observed large three-beam signals at the *potassium D* line, but these represent *red* shifts and additional work must be done to rule out other processes.