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CHEMILUMINESCENT CHANNELS OPENED BY PHOTON ABSORPTION DURING
REACTIVE COLLISIONS

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Abstract - Lasers are used to probe the transient species which exist as reagents are transformed into products in a chemical reaction. Molecular beams of reagents K and NaCl are crossed within the cavity of a cw dye laser and photons absorbed by the transient species are used to open the chemiluminescent channel to KCl and Na + .

I. Introduction

Collisions between atoms are usually described in terms of the potential energy between the atoms, and one can frequently calculate or experimentally determine the potential energy curve as a function of internuclear separation. Numerous examples of such potential curves can be found in other articles in this volume, and their utility in interpreting diverse phenomena can be seen from a perusal of these articles.

Chemically reactive collisions, on the other hand, are much more complicated. First, the simplest reaction involves an atom reacting with a diatomic molecule,

\[ A + BC \rightarrow AB + C \]  

(1)

which is a three (or more) body problem. The choice of coordinate system is complicated by the fact that the final system differs from the initial system. For the "simple" system of reaction 1, the potential energy will depend upon the distance between each pair of atoms, \( r_{AB}, r_{BC}, \) and \( r_{AC} \). The potential energy is thus a surface in four dimensional space which is difficult to imagine. In order to simplify calculations and provide a conceptual basis for discussion, one frequently discusses collinear reactions, where, for example, the atoms of reaction 1 are confined to a line. The potential energy for the system then depends on only two distances, \( r_{AB} \) and \( r_{BC} \) and contour plots can be used to describe the system.

The general form such a contour plot takes is shown in Fig. 1 which is qualitatively similar to the potential energy surfaces (PES) calculated by Eyring and his co-workers in the 1930's. In the asymptotic entrance or exit channels, the canyon in cross section is just the potential curve for a diatomic molecule. As the reagents approach one another, considerable interaction distorts the simple diatomic molecules and the potential energy may rise to a col before descending into the product canyon. The well shown in Fig. 1 originally appeared as an artifact of the calculation for \( \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \), and while it is known that no well exists for \( \text{H} + \text{H}_2 \), reactions such as \( \text{H} + \text{OH} \rightarrow \text{H}_2 + \text{O} \) can clearly have very deep wells corresponding to strongly bound stable molecules. The path of minimum potential
energy, shown as a dashed curve in Fig. 1, is presumed to describe the gross behavior of the system and the potential energy plotted versus distance along this "reaction coordinate" is shown schematically in Fig. 2. Plots of this type are used in qualitative discussion of chemical reactions, but one must bear in mind that plots such as Fig. 2 represent a special two-dimensional cut through a surface of at least four dimensions.

Fig. 1. Potential energy contour plot (schematic) for collinear reaction of A with BC. Dashed line corresponds to minimum energy path.

Fig. 2. Potential energy vs. reaction coordinate (distance along dashed line of Fig. 1) for collinear, thermoneutral reaction of A with BC. Region near top of barrier corresponds to nuclear configurations which are neither reagent nor product and are denoted as "reaction complexes" or "transition states."

The time evolution of a chemical system across the PES is a problem of fundamental interest to chemistry. Experimentally, of course, reactions do take place, and a great deal has been learned about these processes by measuring the rate of evolution from reagents to products. Molecular beam and laser techniques has made possible state-to-state chemistry, the study of how individual quantum states of the reagents affect reactivity and of how the products are distributed among different possible final states. But these techniques examine the asymptotic states of the system. The region of the PES of greatest interest near the col is only indirectly sampled. Theoretical treatment of the time evolution is very difficult because the dynamics (either classical or quantal) of the system are very sensitive to the precise details of the surface, especially near the corner.

In order to provide direct information about crucial regions of the PES, we have tried to spectroscopically interrogate chemically reactive systems in the few picoseconds during the course of the reaction where the system is between reagents.
and products. In this region one has neither reagents nor products but rather a system in which old bonds are being broken and new bonds are being formed. We use the term "reaction complex" or "transition state" to denote these molecular configurations. As suggested in Fig. 2, this region is expected to encompass many nuclear configurations, and is expected to be rather short lived.

II. Experimental Considerations

There are basically three problems associated with studying these reaction complexes: formation of the reaction complex; detection of the reaction complex or its light absorption; and interpretation of the results. We shall discuss the first two problems here and the last in the discussion section.

Formation of the reaction complex is expected on at least each reactive event, but the concentration of complexes which can be obtained is expected to be very low as experimental estimates for the "lifetimes" of such reaction complexes are typically < 1 ps. Further, this concentration is determined in steady state by the competition between the rate of formation of the complex and its rate of decomposition. Thus reactions which occur on every collision are most desirable in terms of producing a high concentration of reaction complexes. This precludes carrying out the reaction in some sort of cell as, even if the formidable problem of mixing the reagents were solved, the reaction would be complete on a very short time scale. To solve the problem of mixing the reagents, the method of crossed molecular beams was adopted. This also has the advantage of eliminating some possible artifacts, such as wall reactions.

The number of reaction complexes excited is expected to be low. 1/ Detecting excitation of the reaction complex is thus quite a non-trivial assignment even with the high photon fluxes obtainable with lasers, and even if the transition probability for exciting the complex is high. As the best chance for accomplishing this, we therefore decided to search for a chemical reaction in which a luminescing product could be formed if the reaction complex absorbed light.

\[ A + B \rightarrow [AB]^+ + h\nu \rightarrow C^* + D \]  

where A and B are generalized reagents (atoms or molecules); \([AB]^+\) is the reaction complex, or transition state; C and D are generalized products; and the asterisk denotes electronic excitation. Excitation of the reaction complex would thus be detected by observing emission of \(C^*\). [Weiner and colleagues 2/ have pursued the other attractive option for solving the detection problem and are carrying out similar experiments involving chemi-ionization in which the detected species is \(C^+\).]

In order to distinguish the excitation of the reaction complex from the much more likely processes involving direct photon excitation of either the reagents or the products the excitation wavelengths must be chosen to avoid exciting any state of the reagents or products. In addition it is most desirable to have the emission wavelength blue-shifted from the excitation wavelength in order to discriminate against energy transfer processes involving minor contaminants of the molecular beams. This can be arranged by having the exoergicity of the reaction supply the energy defect between the energy of the excitation photon and the energy of the emitted photon.

In order to carry out the experiment most efficiently one wishes to maximize the number of \(C^*\) species formed in the time available for observation. The lifetime of the reaction complexes is so short that power saturation is not expected at moderate photon intensities, and the rate of reaction (2) is expected to be linear in laser intensity. Therefore, the highest obtainable average laser power should be used. It is also important not to use lasers with high peak powers in order to avoid, or at least minimize, multiphoton processes. Clearly, cw operation provides
the lowest peak power in combination with the highest average power. At present the highest tunable average power is obtained intracavity in a cw dye laser.

The system selected for the experiments described here is

\[ K^+ + NaCl + h\nu \rightarrow Na^* + KCl \]  

An energy level diagram is shown in Fig. 3 for this system.

Fig. 3. Energy level diagram for K reacting with NaCl. If a reaction complex were to absorb light with \( \lambda \leq 657 \text{ nm} \) the excited complex would have enough energy to decompose to KCl and Na*. (About 3000 cm\(^{-1}\) of thermal energy is also available to the system and the observed threshold is further to the red, \( \sim 740 \text{ nm} \).) Excited Na is detected by emission of the D lines at 589 nm.

This reaction meets the experimental criteria just set forth:

(a) The activation energy is low and reaction occurs on each hard sphere collision. In addition a complex is formed which seems to persist for a few ps.

(b) The reaction is exoergic so blue-shifted chemiluminescence can be observed for wavelengths near threshold.

(c) No single-photon absorptions are known for the reagents or products in the region near the threshold.

(d) Beams of all reagents -- chemicals and photons -- can be "easily" generated.

(e) The threshold photon energy for the new channel occurs in wavelength regions easily accessible to cw dye laser operation.

III. Experimental

The apparatus is more completely described elsewhere /3/ and only a brief summary will be given here: collimated molecular beams cross inside the cavity of a cw dye laser (see below). Fluorescence from the reaction zone (RZ) is collimated, passed through an interference filter to reject wavelengths not resonant with the
fluorescing species (and thereby excluding copious amounts of scattered laser light) and detected with a cooled photomultiplier operated in the pulse-counting mode. The cavity of a Spectra Physics Model 375 dye laser is extended to include the molecular beam apparatus by replacing the output coupler with a mirror 1.5 m downstream from the laser. Cooled solutions of Rhodamine 6G and DCM in soap solution are pumped with the 514.7 nm line of a CR-18 Ar^+ laser. The dye laser is not focussed at the RZ, and has a diameter of about 2 mm there.

The molecular beams contain trace amounts of Na which are excited by the (weak) spontaneous fluorescence of the dye stream at the D line, even if the laser is las-
ing at frequencies far from the Na D line. Therefore, fluorescence from the dye stream at the Na D lines was removed by a small intracavity heat pipe oven containing Na and a few torr of Argon. The laser is tuned by a 3-plate birefringent filter with a bandwidth ~ 1.5 cm⁻¹.

The fluorescence from the RZ was passed through an interference filter centered at 589.0 nm with a band pass of 0.47 nm which passed only the 589.0 nm D line. Some light is emitted from the RZ (scattered light, photoluminescence, etc.) and may still pass through the filter for various beam combinations. In order to account for these various contributions, the K and light beams were chopped at 20 and 90 Hz respectively, and the NaCl beam was interrupted by a beam flag. A LSI-11 mini-computer with Camac interface was used to acquire data in all 8 beam on-off configurations. The signal of interest, the three-beam signal (3BS), is that signal which appears only when all three beams are on.

### IV. Results

Typical results for a counting period of about 5 minutes are shown in Table I. Count rates are shown for various elementary signal processes $R_{ijk}$ where $i, j, k$ are 0 or 1 to indicate K, NaCl or laser, off or on, respectively. These elementary rates are assumed to be additive so that the signal observed with all beams on, $S_{111}$ is given by

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

<table>
<thead>
<tr>
<th>Signal</th>
<th>Origin</th>
<th>Count Rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{000}$</td>
<td>Dark Current</td>
<td>4.2 ± 1</td>
</tr>
<tr>
<td>$R_{001}$</td>
<td>Scattered Light</td>
<td>23.3 ± 2</td>
</tr>
<tr>
<td>$R_{100}$</td>
<td>K Background</td>
<td>0.0 ± 1</td>
</tr>
<tr>
<td>$R_{010}$</td>
<td>NaCl Background</td>
<td>24.2 ± 2</td>
</tr>
<tr>
<td>$R_{101}$</td>
<td>K Photoluminescence</td>
<td>146.4 ± 5</td>
</tr>
<tr>
<td>$R_{011}$</td>
<td>NaCl Photoluminescence</td>
<td>29.4 ± 4</td>
</tr>
<tr>
<td>$R_{110}$</td>
<td>Chemiluminescence</td>
<td>0.0 ± 3</td>
</tr>
<tr>
<td>$R_{111}$</td>
<td>3 Beam Signal (3BS)</td>
<td>559.3 ± 13</td>
</tr>
</tbody>
</table>

The 3BS, $R_{111}$, is positive and highly significant statistically. It should be emphasized that this signal is present only when all three beams are on. If any one beam is missing, $R_{111}$ is zero. This signal is relatively reproducible /4/ and is present over a very wide range of excitation wavelengths. Fig. 4 shows the 3-beam
signal (corrected for drifts and normalized for comparison between different days) versus laser wavelength. The scatter in points does not seem to reflect spectral features, but rather to be due to fluctuations in the intensities of one or more of the beams. As suggested in Fig. 4, a threshold for $R_{111}$ is observed near 720 nm, and preliminary results for the threshold are shown in Fig. 5.

![Graph 4](image4.png)

**Fig. 4.** Three beam signal, $R_{111}$, versus excitation wavelength. Various symbols represent different runs which are normalized to one another. Error bars are ± 1 σ and are shown for various runs. The shaded area represents the average of different runs ± 1 σ.

![Graph 5](image5.png)

**Fig. 5.** Three beam signal, $R_{111}$, versus excitation wavelength in the region near the threshold. Dashed line is for illustration.

The dependence of $R_{111}$ on laser power is shown in Fig. 6. The power was monitored by detecting the vertically polarized light transmitted by the "100% reflecting" end laser mirror; this polarization was not proportional to the horizontally polarized light reflected from the Brewster windows on the beam machine. Since the cavity is spoiled for the horizontal polarization, the vertical polarization is the dominant polarization in the cavity and is the appropriate signal to monitor for the power dependence. (When the wavelength is changed, the vertically polarized component of the reflection off the Brewster windows is monitored because the transmission of the end mirror depends on wavelength.) The laser power was changed by either spoiling the cavity slightly, or by reducing the Ar$^+$ pump laser power.

"K photoluminescence," $R_{111}$, is presumed to arise from K dimers, which are well-known in alkali metal beams, and this photoluminescence is quite large if viewed through a red-pass filter. Excited K$_2$ are thus clearly formed by the laser, and sequential processes involving K$_2$, such as

$$K_2 + h\nu \rightarrow K_2^*$$  \hspace{1cm} (4)

$$K_2^* + NaCl \rightarrow Na^* + K_2Cl$$  \hspace{1cm} (5)

$$Na^* + KCl + K$$  \hspace{1cm} (6)

must be considered (although it should be noted that (6) is not energetically open unless two photons are absorbed which is hard to correlate with the observed linear dependence of 3BS on power, Fig. 6. Because of lack of information regarding the
Fig. 6. Three beam signal, $R_{111}$, versus laser power. The line is drawn through the data.

Bond energies of $K\text{Cl}$, it is impossible to know if (5) is energetically open. Signals were compared for laser excitation on a $K_a$ bandhead and excitation at an adjacent minimum. Even though the photoluminescence varied by a factor of 15, $R_{111}$ varied by less than 10%. We conclude that reaction (5) cannot account for the signal we report.

The 3 beam signal is from the fluorescence of Na atoms, presumably those formed in a chemical reaction. But both beams contain trace amounts of Na impurities and excitation of the impurity Na via sequential energy transfer from an artifact A

$$A + h\nu \rightarrow A^*$$  \hspace{1cm} (7)

$$A^* + \text{Na} \rightarrow \text{Na}^* + A$$  \hspace{1cm} (8)

would appear as a 3 beam signal. Species A cannot be either $K$ or NaCl since no single photon absorptions are known in this wavelength region, nor can it be the $K$ dimer since the 3BS is independent of direct excitation of $K_a$. In order to rule out other, unknown, artifact species, we performed auxiliary experiments on Na + NaCl and $K + \text{Na}$ in which the Na beam was adjusted to be comparable to Na intensities in the main experiments. In both cases the chemical reaction $K + \text{NaCl}$ is removed, but the possibility of energy transfer from some impurity is still present. No 3BS is observed under these other conditions, and we conclude that such an artifact source can be ruled out.

V. Discussion

Fluorescence is observed from the region of the overlap of molecular beams of $K$ and NaCl which cross inside the cavity of a cw dye laser. This fluorescence is highly statistically significant and arises from the emission of an excited sodium atom, Na$^*$. Because of the low densities in the molecular beams, the process responsible for these signals most likely involves binary molecular collisions between species from each molecular beam. Wall effects and secondary collisions may be ruled out, and we interpret the process responsible for these signals as the laser assisted reaction

$$K + \text{NaCl} + h\nu \rightarrow \text{KCl} + \text{Na}^*$$  \hspace{1cm} (3)
Our interpretation is based on the following experimental observations:

(a) The signal occurs only when all three reagents are present. All one- and two-beam contributions to the signal (e.g., dark current, scattered light or photoluminescence, etc.) have been subtracted from the raw signal.

(b) The signal is linear in laser intensity which suggests that only one photon is responsible for this process.

(c) No single photon absorptions are known in this wavelength range for either the reagents (K, NaCl) or the products (Na, KCl).

(d) The signal is due to fluorescence at the Na D line and is assumed to be due to Na.

(e) The signal (emission of Na*) is observed over a wide range of exciting wavelengths. This emission is blue shifted from the exciting light.

(f) The signal is linear in NaCl intensity and appears to be linear in K intensity.

Observation of reaction (3) is consistent with all of these observations. We have not been able to think of any other process which is consistent with all of the experimental facts, and we conclude that we have observed the laser-assisted reaction

$$K + NaCl + h\nu \rightarrow KCl + Na^*$$

The reaction exoergicity can provide the energy required for the blue-shifted emission, and energy balance requires

$$\varepsilon_i + \varepsilon_t + h\nu_L + AD_0 = \varepsilon_i^* + \varepsilon_t^* + \varepsilon_0^*$$

where \(\varepsilon_i\) and \(\varepsilon_i^*\) denote internal energy and translational energy respectively, primes denote reaction products, \(h\nu_L\) is the frequency of the laser, \(AD_0\) is the difference in dissociation energies of products and reagents, \((1750 \pm 1000 \text{ cm}^{-1})\) and \(\varepsilon_0^*\) is the energy of the Na D line \((16,970 \text{ cm}^{-1})\). The threshold laser energy will occur when \((\varepsilon_i + \varepsilon_t^*) \approx 0\), so \((h\nu_L)_{\text{threshold}} = \varepsilon_0^* - (\varepsilon_i + \varepsilon_t) - AD_0\). \((\varepsilon_i + \varepsilon_t)\) can be approximated by the thermal energy, \(~3350 \text{ cm}^{-1}\) so \((h\nu_L)_{\text{threshold}} = 11,870 \pm 100 \text{ cm}^{-1}\). The experimental threshold at 740 nm is consistent with this value because it is unlikely that all of the thermal energy can be utilized in the blue shift. (Rotational energy of the diatomic is likely to be roughly constant to conserve total angular momentum, for example.)

In the absence of laser light, crossed molecular beam experiments \(5/\) have been shown that the ground state reaction

$$K + NaCl \rightarrow [KNaCl]^* \rightarrow KCl + Na$$

proceeds on nearly every hard-sphere collision. The angular distributions of the products shows that a complex, \([KNaCl]^*\), is formed which persists for a few rotational periods. Pseudopotential calculations \(6/\) for the KNaCl electronic surface suggest a bound well in the ground state about 4500 cm\(^{-1}\) deep for bent geometries and classical trajectory calculations \(7/\) on this surface suggest that most reaction occurs through triangular complexes with lifetime 2 - 3 psec. Thus, while reaction (3) can be considered as a simultaneous three-body collision, we prefer to regard reaction (3) as a reaction in which the reaction complex, or transition state, is excited by a photon:
We thus view this process as a "sticky collision", followed by a conventional light absorption process. (At the power levels used, \( \sim 3 \text{ kW/cm}^2 \), the laser presumably probes the electronic potential energy surface, whereas much higher intensities are required before the laser could perturb those surfaces.) The absorption process differs from that which occurs in conventional spectroscopy in more important ways, however. Electronic transitions are likely to occur from a wide range of nuclear configurations (a large area on the ground PES), rather than from a few well-defined nuclear configurations as in conventional absorption spectroscopy. This comes about for several reasons. First, the reaction complex (absorbing species) has a very short lifetime, and second, the complex will sample many different nuclear configurations as it evolves from reagents to products. Third, the complexes are formed with a large distribution of energies and angular momenta. Thus these experiments do not probe a single point on the PES ("The" transition state corresponds experimentally to a range of nuclear configurations.)

The spectrum reflects the energy difference between the upper and lower PES for the system. Several generalities can be expressed. If the system spends more time in a small region of the PES, the spectrum would be expected to display a maximum at wavelengths corresponding to the separation between the surfaces for the confinement region. Likewise, if the surfaces are "parallel" over a range of configurations, a different type of maximum would be obtained as a result of many configurations being capable of absorbing photons of essentially the same wavelength.

Although the signal-to-noise so far is insufficient to be certain, the experimental spectrum does not seem to exhibit any features. It is possible that the very high effective "temperatures" of the complexes which would average out any such features. It is also possible that the PES are of the wrong selective slopes for the formation of structure. Fig. 7 shows a section of the first three collinear PES obtained from pseudopotential calculations by Roach and Child. /6/ For the 180° approach (collinear) there is no well in the ground surface, but for bent geometries a well appears; changes are also expected for the excited states in bent geometries. The ground and excited state curves are rather dissimilar and it seems likely that an optical transition would result in a fairly wide absorption band because the Franck-Condon transition probabilities are expected to be relatively constant (and relatively small) over a wide range of wavelength.

These experiments demonstrate that direct spectroscopic observation of a system in the process of chemical reaction is possible. What have we learned and what direction should future work take? First, in terms of the particular reaction studied here, the entire picture is consistent qualitatively with the nature of ground and lowest excited potential curves of Roach and Child which have very different shapes and would therefore be expected to give rise to a broad spectrum. Also because the excited state and ground state curves are related by an avoided crossing between two different kinds of ionic curves, it is reasonable to expect a very large electronic dipole transition moment. This is at least reassuring. Experimentally, it is logical to investigate some similar systems such as Rb + NaCl in order to look for systematic changes. The pursuit of structure in the spectrum could be advanced by using reactant beams cooled by supersonic expansion in order to remove thermal energy from the reagents. A interesting possibility is introduced by tuning the laser to the red of the K D lines where the excited state of the complex is bound, then looking for blue-shifted bound-bound fluorescence into the lower state potential well.
Fig. 7. Potential energy vs. reaction coordinate for collinear K + NaCl reaction. Curves b and c approximate the minimum energy path on the ground state surface for KNaCl angles of 135° and 90°, respectively.

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References


