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COMMUNICATIONS

Effect of atomic reagent approach geometry on electronic state branching: The $\text{Ca}(^1P_1) + \text{HCl}$ reaction^{a)}

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That the geometry of reagent approach should influence the outcome of a bimolecular reaction seems intuitively obvious. However, state preparation at this level presents a severe experimental challenge, and only a relatively few studies have been carried out to date. These have employed one of two techniques. In most cases, hexapole fields have been utilized to orient polar molecules¹⁻³ while more recently it has been shown that photoselection can be employed to produce aligned excited-state reagents.^{4,5} Here we report a study based on this latter approach, in which we have investigated the influence of the alignment of the laser-excited $\text{Ca}(^1P_1)$ reagent on the outcome of the (previously unreported) chemiluminescent reaction $\text{Ca}(^1P_1) + \text{HCl} \rightarrow \text{CaCl}(A^2\Pi, B^2\Sigma^+) + \text{H}$. We find that while the total chemiluminescence cross section is relatively insensitive to atomic alignment, the branching into these two CaCl^* states depends quite strongly on the approach geometry.

The above reaction is well-suited to such a study for two reasons. First, reaction on the ground-state surface is ~ 38 kJ/mole endothermic; hence interference by laser-induced fluorescence from the ground-state $\text{CaCl}(X^2\Sigma^+)$ product⁶ is not expected. This is supported by our finding that signals are only observed while the laser is tuned to the atomic transition $\text{Ca}(^1S_0 \rightarrow ^1P_1)$. Secondly, the polarization of the chemiluminescence from this reaction is highly kinematically constrained^{7,8} and cannot be appreciably effected by reagent approach geometry. Hence changes in detected intensity can be attributed to changes in overall photon emission, without consideration for its distribution.

The apparatus is basically the same as that described previously.⁶ Briefly, a Ca beam impinges on a HCl scattering gas at $\sim 10^{-4}$ Torr. The $\text{Ca}(^1S_0 \rightarrow ^1P_1)$ transition at 422.6 nm is pumped by a multimode linear dye laser, producing 300 mW over a bandwidth of ~ 1 cm⁻¹. Chemiluminescence is collected at 90° to both the laser and the metal beam axes using a single glass lens. A cut-off filter transmitting only to the red of 440 nm is placed in front of this lens to exclude detection of scattered atomic emission. The lens images the fluorescence onto the (1 mm) slits of a 1 m monochromator for ultimate detection on a cooled photomultiplier. Maximum signals

$\sim 10^{-8}$ A are obtained. In addition, a separate photomultiplier views the atomic emission at 90° to the laser, but at an angle of 45° to the metal beam.

The **E** vector of the linearly polarized dye laser output is rotated by passage through two optically contacted back-to-back Fresnel rhombs. By spinning this assembly at 2.5 Hz, the **E** vector is caused to rotate at four times this frequency. A reference signal from this assembly triggers the sweeps of a signal averager (Nicolet 1170 with 171/2 plug-in) on which all data are recorded following preamplification. Care is taken to ensure that the laser intensity at the reaction zone is independent of polarization.

The chemiluminescence spectrum obtained at a resolution of ~ 1 nm is very similar in appearance to that reported previously for the $\text{Ca}(^1D_2) + \text{HCl}$ reaction.⁹ Running this reaction on our apparatus we find the most significant difference to be an approximately twofold increase in the $B^2\Sigma^+$ channel relative to the $A^2\Pi$ product in the case of the $\text{Ca}(^1P_1)$ reagent. Note that the 1D_2 state can be populated by radiative cascade from the 1P_1 state. However, this process is so slow¹⁰ that build up of 1D_2 atoms is negligible under our conditions.

Figure 1 displays various signals obtained as a function of the rhomb assembly rotation angle. Four traces are shown, labeled (a)–(d), each of which was recorded using the signal averager. Trace (a) shows the (essentially flat) response of a power monitor (photodiode placed behind a polarization scrambler) positioned to observe the laser intensity as it emerges from the flat exit window. Traces (b) and (c) show the variation in chemiluminescence intensity from the $\Delta v = 0$ sequences of the $\text{CaCl } A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ bands, respectively. The zero for these traces (laser blocked) is found to coincide with trace (d), obtained in the absence of HCl scattering gas. Defining a laser polarization quantity $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} are intensities obtained with **E** parallel and perpendicular to the average relative velocity vector, we obtain $P_{A-X} = -0.039 \pm 0.003$, whereas $P_{B-X} = 0.074 \pm 0.005$. Concurrent measurements on the $\text{Ca}(^1S_0 \rightarrow ^1P_1)$ line yield $P_{S-P} = 0.96 \pm 0.005$, which is close to the value obtained for the laser beam itself.

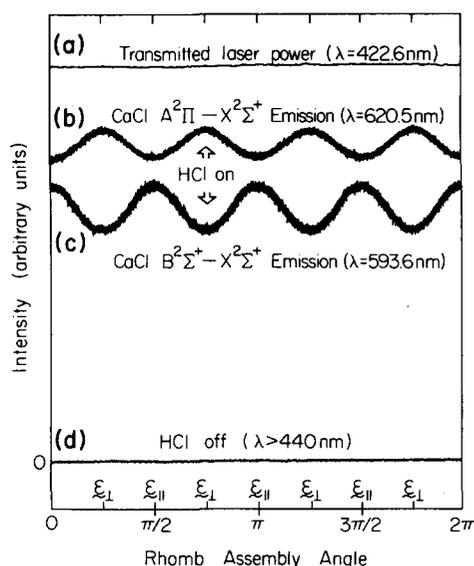


FIG. 1. Variation with rhomb assembly angle of (a) the transmitted laser power, (b) the $\text{CaCl } A^2\Pi-X^2\Sigma^+$ chemiluminescence ($\Delta v=0$ sequence), (c) the $\text{CaCl } B^2\Sigma^+-X^2\Sigma^+$ chemiluminescence ($\Delta v=0$ sequence), and (d) the signal observed in the absence of HCl reagent but with other conditions as in (a)–(c). E_{\parallel} and E_{\perp} denote the positions where the electric vector of the laser beam is pointed parallel to and perpendicular to the average relative velocity vector of the reagents, respectively.

Thus we find that switching from E_{\perp} to E_{\parallel} enhances the $\text{CaCl}(B-X)$ emission by $\sim 16\%$ while causing the $\text{CaCl}(A-X)$ emission to decrease by $\sim 7\%$. Since we find the integrated $A-X$ intensity to be about 2.5 times that of the $B-X$ intensity, the smaller percentage change in $A-X$ emission acts to roughly cancel the larger change in the weaker $B-X$ emission.

Before commenting further on these results, we note the extent to which we have *failed* to control the collision geometry: (i) the beam-gas relative velocity is only confined to $\sim 20^\circ$ under our conditions,¹¹ (ii) the impact parameter for the collision will vary, causing further averaging of the orbital alignment in the molecular

frame, and (iii) the initial orientation of the HCl target is random. Accepting this, it is apparent that the effects reported represent a high degree of steric selectivity at the molecular level.

A simple molecular orbital picture may account for the dependence of the electronic-state branching ratio on reagent approach geometry. We propose that the p orbital of the Ca atom becomes the $p\sigma$ or $p\pi$ orbital of the excited CaCl molecule.¹² Thus, when the p orbital points toward (perpendicular to) HCl it is preferentially transformed into the $p\sigma(p\pi)$ orbital, favoring the formation of the $\text{CaCl } B^2\Sigma^+ (A^2\Pi)$ state. At small impact parameters a given laboratory alignment is approximately retained in the body-fixed frame, which is consistent with our findings. However, for larger impact parameters, the correlation may switch,¹³ showing that the observed electronic branching ratio need not be a general result.

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