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LETTERS TO THE EDITOR

COMMUNICATIONS

Chemiluminescence during the course of a reactive encounter; $F + Na_2 \rightarrow FNaNa^{\ddagger*} \rightarrow NaF + Na^{*a)}$

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There have been a number of theoretical studies[1-3] and a first experimental investigation[4] of the possibility of altering reactive cross sections by laser irradiation of the reaction intermediate. It has been suggested[5] that the most promising starting point for "spectroscopy of the transition state" lies in the measurement of "pressure broadening" due to the collision which constitutes chemical reaction.[5] The example discussed in this earlier Communication[5] is the subject of the experimental results reported here; the reaction $F + Na_2 \rightarrow FNaNa^{\ddagger*} \rightarrow NaF + Na^*(3\,^2P)$ should lead not only to the well studied D-line chemiluminescence (intensity I_{Na^*}) but also to emission in the far wings of the D line, ($I_W(\lambda)$) while Na* is still in range of NaF, i.e., $FNaNa^{\ddagger*}$ is the emitter.

The effective lifetime of $FNaNa^{\ddagger*}$ is $\tau^{\ddagger*} \sim 10^{-12}$ sec,[6] as compared with the lifetime of Na*, $\tau_{Na^*} \sim 10^{-8}$ sec, hence the ratio $\int_\lambda I_W(\lambda)/I_{Na^*}$ (total wing intensity relative to D line), neglecting variation in transition moment, should be $\sim 10^{-4}$.[7] If we view the wing with a spectrometer that divides the major part of the emission into ~ 100 spectral elements, we would be recording intensities $\sim 10^{-6} \times I_{Na^*}$. Accordingly we have set up a crossed uncollimated "beam" apparatus[8] in which F from a microwave discharge in 5% CF_4 + 95% He is crossed with 8% Na_2 + 92% Na.[9] Using a double monochromator (Jarrell Ash, 25-102) and cooled photomultiplier (ITT FW 130) we obtained $I_{Na^*} \sim 10^6$ counts/sec and observed wings (Fig. 1) extending several hundred Å from the D line, with an intensity $I_W(\lambda) \sim 1$ count/sec at a spectral slit width of 8.5 Å.

Several measures of scattered light ensured that the wings were not due to this cause. Next we considered the possibility that the wings were caused by a "secondary" process: Na^* + gas collisions *subsequent* to the reaction.[10]

From measured flows and geometry the concentrations of collision partners in the 0.5 cm³ zone being viewed were $[Na] \approx 1 \times 10^{12}$. $[Na_2] \approx 1 \times 10^{11}$, $[He] \approx 5 \times 10^{12}$ and $[F] \approx 2 \times 10^{10}$ molecules/cm³. These concentrations are consistent with the observed D-line emission intensity.

From the experiments of Gallagher and co-workers it is known that these pressures of collision partners ($\sim 1 \times 10^{-4}$ Torr Na, $1 \times \sim 10^{-5}$ Torr Na_2, $\sim 2 \times 10^{-4}$ Torr He, $\sim 1 \times 10^{-6}$ Torr F) are orders-of-magnitude below the minimum required for the observation of secondary far wing emission.[10] Simple calculations confirm this; at our pressures $\sim 10^{-8}$ of the Na* is, at any instant, within range of a collision partner, hence $\int_\lambda I_W(\lambda)/I_{Na^*}$ due to
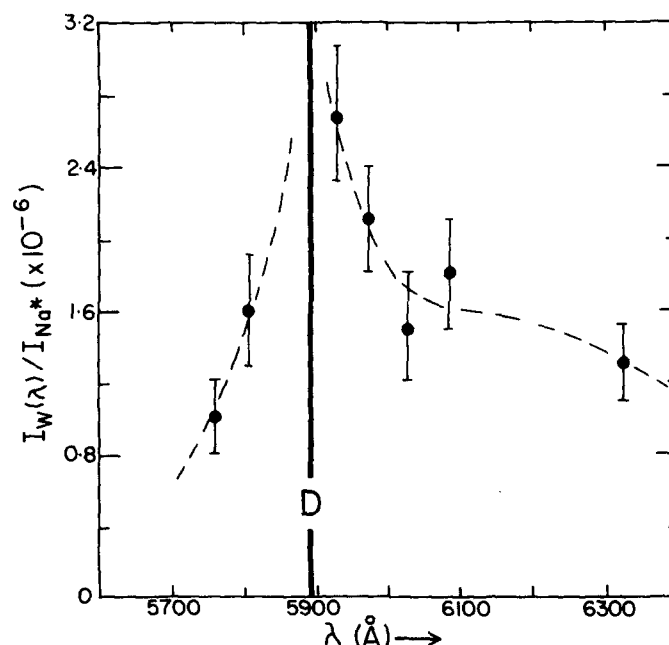

FIG. 1. Wings of the sodium D lines ($D_2 = 5890$ Å, $D_1 = 5896$ Å) recorded at a $D_2 + D_1$ intensity $I_{Na^*} = 2.4 \pm 0.2 \times 10^6$ counts/sec. Each point on the wing represents ~ 300 counts repeated once or twice; error bars give $\sim 1\sigma$ deviation. Intensities were corrected for instrument sensitivity.
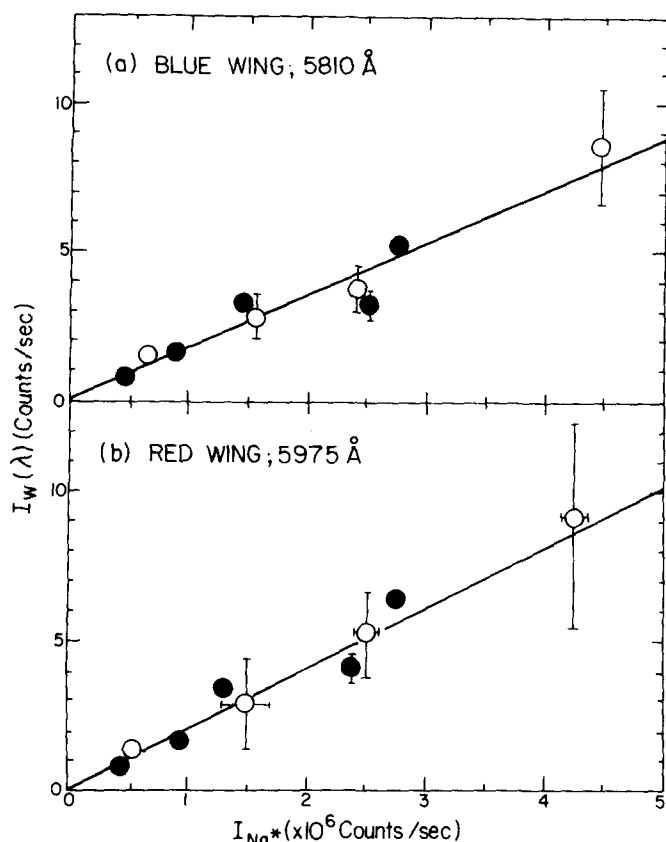
FIG. 2. Dependence of wing intensity, $I_W(\lambda)$, on D-line intensity, $I_{Na}*$. Open circles were obtained in an earlier experiment; the error bars indicate uncertainty in correction for oven thermal radiation. Filled circles, obtained at a later date, refer to experiments with a shielded oven; the statistical uncertainty lies within the points unless otherwise indicated.

may be formed by the slow reaction $F_2 + Na_2 \rightarrow NaF*$ $+ NaF$.[12,13] It is highly unlikely that $NaF*$ (emission spectrum unknown) would *by chance* give rise in our system to emission centered on the D line.[14] If, therefore, molecular emission is responsible for the wings centered at 5890 Å the emitter must have been formed and subsequently excited in a collision with $Na*$ ($E \rightarrow E$ transfer). Ground state NaF is principally formed in the $F + Na_2$ reaction. The hypothetical $E \rightarrow E$ transfer would be $Na* + NaF \rightarrow Na + NaF*$. There is, however, no evidence in studies performed at much higher pressures for this process.[15] The kinetics of such processes would moreover lead to a nonlinear dependence of I_W on $I_{Na}*$ (cf. Fig. 2).

By altering our viewing angle we found the contribution to the wings from surface reaction to be undetectable.

We conclude that the wing emission is a consequence of the primary process $F + Na_2 \rightarrow FNaNa^{\ddagger*} \rightarrow NaF$ $+ Na*$.[12,16,17]

The predominance of the red wing was anticipated[5] since the upper and lower potential-energy surfaces are expected to approach one another more closely in the intermediate configurations $FNaNa^{\ddagger*}$ (upper surface) and $FNaNa^{\ddagger}$ (lower) than at their outruns, $NaF + Na*$ and $NaF + Na$.

Refined measurements of this general type should provide a more stringent test of reaction dynamics than has been available heretofore since the intensities $I_W(\lambda)/I_{Na}*$ embody information concerning the relative times that $FNaNa^{\ddagger*}$ spends at successive configurations en route to $NaF + Na*$.

"secondary broadening" is $\sim 10^{-4}$ times that observed, and calculated, for the primary process.

It is necessary to distinguish secondary broadening from secondary collisions in which $Na*$ transfers its energy to a collision partner that emits subsequent to the encounter. One such process is well known: $Na* + Na_2 \rightarrow Na + Na_2^{\ddagger}$.[11] The $Na_2^{\ddagger}$ emits in a series of well-defined bands ~ 60Å apart. At the higher Na_2 pressures used in this work $Na_2^{\ddagger}$ bands were detectable; the points in Fig. 1 were chosen to lie between them. As a check that the process $Na* + Na_2 \rightarrow Na + Na_2^{\ddagger}$ made a negligible contribution to the observed emission intensity at these intermediate wavelengths we investigated the kinetics for one point in the red wing and one point in the blue wing (Fig. 2). The abscissa in Fig. 2 gives a measure of the reaction rate to yield $Na*$. It was varied by altering the sodium oven temperature from 830–890 °K. If the wing intensity is governed by $[FNaNa^{\ddagger*}]$ formed en route to $Na*$, then $I_W(\lambda) \propto I_{Na}*$. This is observed to be the case. At $I_{Na}* > 10^7$ counts/sec the curve was no longer linear; $I_W(\lambda)$ approached a quadratic dependence on $I_{Na}*$. We conclude that $Na_2^{\ddagger}$ made a negligible contribution to the wing emission under the conditions of Fig. 1 ($I_{Na}* \approx 2.4 \times 10^6$ counts/sec).

Other emitters need to be considered. Some $NaF*$

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[7]This ratio is insensitive to radiation trapping; in the absence of trapping $I_W/I_{Na}* = A\tau^{\ddagger*}/A\tau_{Na}*$ ($A \equiv A$ − factor) and in the presence of trapping $I_W/I_{Na}* = A\tau^{\ddagger*}/A'\tau'_{Na}*$ where $A'\tau'_{Na}* = A\tau_{Na}*$. We expect only moderate "trapping" since $Na*$ formed chemically is Doppler broadened relative to the thermal Na inflow.
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Phys. **60**, 4032 (1974).

[14]We observed emission centered at 5000 Å with intensity comparable to I_W; this could be due to NaF*.

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[17]There is long-standing debate as to which of the transition states $Na_2F\dagger$* precedes the formation of NaF + Na*. An alternative route involves $NaF\dagger + Na \rightarrow Na_2F\dagger$* $\rightarrow NaF + Na$*; i.e., $V \rightarrow E$ transfer. In work under way we shall attempt to ascertain whether this transition state configuration is contributing to the observed wings.

Mode dependent enhanced vibrational relaxation in low energy He–¹B₂ aniline collisions

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We have previously shown[1] that very low energy collisions between a He, Ne, or Ar atom and a $^3\Pi_{0_u^+} I_2$ molecule in an excited vibrational state lead to extremely fast vibrational relaxation. The very large cross section for this process has been attributed to the lengthening of the collision duration by scattering resonances. In this Communication we report the observation of mode dependent enhanced vibrational relaxation of an electronically excited polyatomic molecule via a low energy collision with an atom. The system we have studied is He – $^1B_2$ aniline; the technique employed is supersonic jet spectroscopy.

Both the apparatus and the data acquisition procedure are the same as in our previously reported work[1] except for those modifications made necessary by the fact that aniline is a liquid, that it has a significantly shorter lifetime than $^3\Pi_{0_u^+} I_2$, and that it absorbs in the ultraviolet region of the spectrum. In the experiments reported herein stagnation pressures (p_0) up to 1000 psi were used with a pulsed nozzle operated at 30 Hz (open time ~1.5 msec). The excitation source bandwidth was typically 0.1–0.2 cm⁻¹. The emission spectrum was dispersed and multiplex detected at the focal plane of a spectrograph using a cooled SIT tube (PAR EGG 1254).

The spectra of the He : $^1B_2$ aniline van der Waals complex are shifted from that of the bare $^1B_2$ species, so it is possible to excite the latter cleanly. For each vibrational level of $^1B_2$ aniline pumped a reference emission spectrum, taken under collision free conditions with p_0 = 50 psi, was recorded. Then, for p_0 large enough to give one collision per lifetime (or more, as needed) emission spectra were recorded for several values of $1 \leqslant \hat{x} \leqslant 8$, were $\hat{x}$ is the displacement downstream from the nozzle measured in nozzle diameters.

Typical emission spectra for the cases that the I^2 and 1^1 levels of $^1B_2$ aniline are pumped are displayed in Fig. 1. Since the relative He – $^1B_2$ aniline collision energy decreases as $\hat{x}$ increases, these spectra show that the level 1^1 can be depopulated by much lower energy collisions than can the level I^2. We find that redistribution of energy from I^2 and $6a^2$ requires collision energies up to about 20 cm⁻¹, from 12^1 and $6a^1$ collision energies up to about 10 cm⁻¹, whereas for 1^1 it can be accomplished by collisions with energy less than 5 cm⁻¹.

An equally important qualitative observation concerns the pathways of collision induced energy redistribution. An incomplete set of assignments is the following: $0^0 \rightarrow$ no energy transfers; $6a^1 \rightarrow I^1$ and 0^0; $I^2 \rightarrow 0^0$ only; $1^1 \rightarrow 16a^1 \ 10b^2$; $12^1 \rightarrow 0^0$, I^1 and possibly $10b^3$; $6a^2 \rightarrow 0^0$, $16a^1 \ 10b^2$ and possibly $16a^1$, $16a^1 \ 10b^1$, and $I^2 \ 10b^1$. The term "possibly" is used to imply that although the observed emission frequencies fit the assignments, the available data are insufficient to make the assignments definitive.

Chernoff and Rice[2] studied collision induced intramolecular redistribution of vibrational energy in $^1B_2$ aniline. The only initial states which they and we both prepared are $6a^1$ and 0^0. When it is recognized that for $\hat{x} > 2$ the collision energy in the jet is too low to permit up-pumping from $6a^1$, comparison of the two data sets reveals that no new levels were populated via the low energy collision. Since there are many levels with energy less than $6a^1$ which are not involved in the collision induced relaxation process, this is a strong conclusion. A weaker inference can be drawn from the observation that up-pumping from the level 0^0 is not seen even for $\hat{x} \simeq 0.5$ where the fraction of collisions with energy ~ 200 cm⁻¹ is significant, while in the room temperature experiments Chernoff and Rice see $0^0 \rightarrow 10b^1$ (177 cm⁻¹), $16a^1$