Oscillations of the *D* line emission in shock generated sodium halide plasmas

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Charge neutralization in ionic collisions selectively produces excited atomic states with very large sections;[1-4] e.g., $Na^+ + O^- \rightarrow Na(3d) + O(^3P)$ exhibits a cross section of order 10^{-13} cm^2 over the energy range 0–7 eV. The reaction is nearly resonant, but slightly exoergic with a crossing distance of 288 Å. Production of Na $3p$ is believed to have a much smaller cross section, more nearly consistent with its ~10 Å crossing distance.

These results suggest the possibility of obtaining atomic population inversions by means of ion neutralization reactions. Tsibilov *et al.* observed alkali–H_2 discharges; they reported low-power superradiance on the Na lines at 11 404 and 11 382 Å and on the *K* lines at 12 434 and 12 523 Å, and attributed their results to reactions such as $Na^+ + H^- \rightarrow Na(4s) + H$. High concentrations of halide ions can be produced by the thermal dissociation of halides of heavier alkalies, behind shock waves.[6-8] From 2500 to 4000 °K the primary dissociation of these molecules proceeds overwhelmingly by the ionic route.

This work is a step toward extracting coherent light energy from these ionic–atomic inversions. Curve crossings in the reaction

$$Na^+ + I^- \rightarrow Na^0 + I^0, \tag{1}$$

lead to the atomic limits Na $3s + I^2P_{3/2}$, Na $3s + I^2P_{1/2}$ and Na $3p + I^2P_{3/2}$. The latter is almost isoergic with the ionic limit, and by analogy with the Na^+–O^- system very large cross sections are expected for the production of Na $3p$. In contrast the sodium salts of other halogens (with higher electron affinities) do not exhibit crossing to the excited states of Na.

Below 6000 °K the Na *D* emission from shock heated NaI vapor corresponds closely with the low temperature results of Berry,[6] Mandl,[7] and Troe *et al.*[8] Rapid electronic excitation of the metal is followed by a slower decrease in intensity as ionization occurs. This characteristic overshoot has been observed in Cs,[9] Ti,[10] and Cr[11] vapors. We observed it in NaCl vapor at temperatures as high as 10 000 °K.

However, in NaI above 7000 °K, additional features appeared in the time evolution of the Na *D* intensity (Fig. 1). Strong emission appears 30 μsec after the arrival of the reflected shock. Similar behavior is found in shocks with Na salts in CsI vapor.

Interpretation of this behavior requires a knowledge of the rates of the reactions

$$Na^0 + e^- \rightarrow Na^+ + 2e^- \tag{2}$$

$$I^- + e^- \rightarrow I^0 + 2e^- . \tag{3}$$

(Dissociation is virtually complete in the incident shock and is irrelevant here.)

Unfortunately the rates of Reactions (1)–(3) above 5000 °K are unknown. The best that can be done is to employ rather uncertain extrapolations from the low temperature data, for which we used the rate constants of Milstein and Berry.[12]

With salt concentrations of typically 10^{16} cm^{-3}, electron concentrations of 10^{14-15} cm^{-3} occur in the incident shock region. With an atomic ionization rate constant $k_{ion} \sim 10^{-9}$ cm^3 sec^{-1} the effective ionization relaxation time will be about 1–10 μsec. As the electron concentration increases, Reactions (2) and (3) are subject to autocatalysis. The figure of 10 μsec is somewhat less than the observed "induction" time in Figs. 1 and 2, but

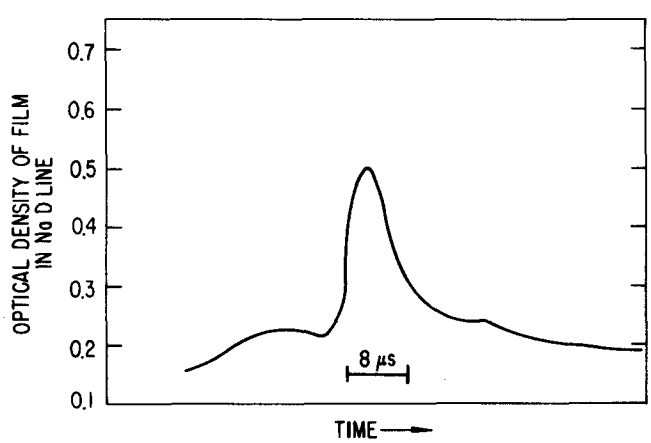

FIG. 1. Densitometer trace of *D* line emission from a pure NaI shock: $P_1 = 20$ torr, $P_5 = 5.5$ atm, $T_2 = 3200$ °K, $T_5 = 7200$ °K.

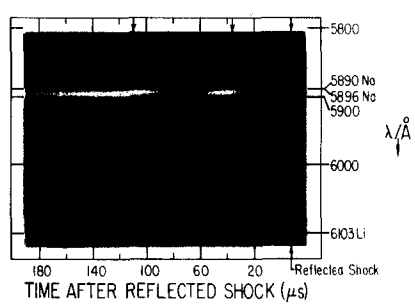

FIG. 2. Time resolved spectrum of Na *D* emission from NaCl + CsI mixture, $P_1 = 32$ torr, $P_5 = 10.3$ atm, $T_2 = 3600$ °K and $T_5 = 8200$ °K. Arrows denote maxima in the emission intensity.

given the uncertainties in concentrations and rate constants, the agreement is satisfactory, and we proceed under the assumption that the rapid increase in the D line intensity after 20–40 μsec is directly related to the onset of ionization. For the halide ion Reaction (3) the corresponding relaxation time is one hundred times longer; consequently the halide ion is initially in excess in the reflected shock region. The relaxation of this excess will proceed via Reaction (2) followed by Reaction (1). *It is believed that the* I^- *excess provides the driving force for the oscillations seen in the reflected shock region.* For Na^+-I^- collisions Reaction (1) is very fast, producing Na in the excited state which is then emitted. The overshoot in Fig. 1 is preceded by a dip in the Na D emission intensity, suggesting the onset of ionization. For other sodium–halogen systems there is no crossing to an excited state of Na, so that the Na emission intensity cannot increase, and the ion neutralization rate is very much lower than with Na^+-I^-.

Frequently the observed D line behavior departs from the simple form described thus far. In particular the single overshoot is replaced by multiple oscillations which begin at about the same time as the overshoot, but persist for up to 100–200 μsec afterwards (Fig. 2). The peaks in these oscillations are weaker than the single overshoot peak but for shocks fired under similar conditions, the total area under the peaks is similar. Moreover, the peaks exhibit a definite red shift as time increases, implying a time-dependent charge concentration during the 20–30 μsec of each peak.

When excess iodide is introduced as CsI, the kinetics are similar except in the immediate post-shock region where a short-rapid overshoot sometimes occurs. This is presumably associated with the dissociation of a little CsI left in the incident shocked gas.

Does the overshoot constitute an inversion or not? Assuming that the ground state population is hardly disturbed by the production of Na in the $3p$ state, we estimate from the spectra that electronic temperatures approaching infinity, but not negative, are produced.

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COMMENTS

Possible tests of tricritical behavior in classical multicomponent mixtures

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We would like to present here a few suggestions inspired by the recent work of Widom[1,2] and Griffiths[3] on the tricritical properties of classical multicomponent mixtures. There, the tricritical point (TCP) is of the nonsymmetrical type, as opposed to the symmetrical TCP found in isotopic helium mixtures and in metamagnets.[4,5] The crossover effects and "subsidiary like" exponents[4] are richer, and one has direct access to the field conjugate to the order parameter Ψ. However, the critical exponents associated with Ψ are expected to be the same as for a symmetrical TCP, both in the tricritical region and in the three-phase coexistence region. These two "canonical" paths of approach to the TCP will be indexed by "t" and "τ," respectively, as in Ref. 5. The exponents themselves will be given their standard notation, and t will stand for $|T - T_t/T_t|$.

In the Landau model,[4] the three exponents describing the collapse of the three-phase coexistence region on approach to the TCP are 3/2, 1, and 1/2. The first

