Anomalous emission in the blue wings of sodium and rubidium lines

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(Received 18 August 1976)

Absorption spectroscopy of the high temperature shock heated vapors of Rb and Na has shown that certain lines of these metals may appear partly in absorption and partly in emission. The lines concerned are the 5890/5896 Å doublet of Na, and the Rb lines at 6298, 6206, 6160, 6071 Å. In all cases the anomalous emission arises in the blue "wing" of the line. Mechanisms to account for this phenomenon are put forward.

EXPERIMENTAL

Time resolved visible spectroscopy of shock-heated rubidium iodide (containing trace quantities of Na) was carried out using the apparatus described by Berry *et al.*[1] The spectra were recorded on Kodak 103-F spectroscopic film using a drum camera capable of a time resolution of about 2 μs.

Shocks were fired into smokes of the halide generated by heating small quantities of salt on a nickel filament situated in the observation region of the tube. Argon was employed as a carrier gas at an initial pressure between 20 and 60 torr. Salt vapor concentrations in the range of 10^{-3}–10^{-2} mole fraction were formed in this way.

Reflected shock temperatures were in the range 5000–11 000 °K, corresponding to incident shock temperatures of 2500–5000 °K. Earlier work has shown that the smoke particles vaporize in less than 1 μs at 1500 °K, and that dissociation of salt and subsequent chemical relaxation takes less than 30 μs at 4000 °K. The incident shock dwell times in the present series of experiments were in the range 20–30 μs laboratory time, or 60–100 μs in the gas frame, so that reaction at the incident shock temperature is essentially complete prior to reflected shock heating.

RESULTS

A typical time-resolved spectrum is shown in Fig. 1. The absorption by the Na *D* doublet is seen quite clearly in the incident shock. On arrival of the reflected shock, the *D* line passes into weak emission which relaxes to absorption, finally emitting again as the flash lamp fades after 200 μs or so. The feature of interest is the strong blue wing which appears in the post shock region, and persists for the duration of the flash even when the *D* line proper is in absorption. Significantly, the blue wing emission is not visible in the emitting *D* line after the lamp emission has faded. The displacement of this wing from the *D* line is apparent; wavelength estimates using Rb lines as reference points put its peak at 5880 Å.

Similar effects were found in the Rb lines at 6298 Å, 6206 Å, 6160 Å, and 6071 Å (although the low intensity of the last line in particular makes definite statements on this point difficult). (See Fig. 2.) Interestingly, the Rb 5724 Å line did not show any tendency to form a blue wing emission; see Fig. 2. Conditions favoring the formation of the Na *D* strong blue emission were similarly effective in producing Rb emission. Optimum conditions were found to be at initial pressures of 20–40 torr and temperatures of 7000–8000 °K. At both lower, and higher, temperatures the incidence of blue wing formation was significantly reduced. Figure 3 shows a densitometer trace of the film shown in Fig. 1. The development of the line shape with respect to time is seen quite clearly. Spectra taken of Na alone in argon show only the normal satellites at their usual wavelengths, well away from the maxima of the "anomalous" blue wing emission.

DISCUSSION

The most interesting feature of Figs. 1 and 2 is the suggestion that the background emission may be exhibiting gain in the blue wings of certain lines on passing through the hot gas. The existence of the emission clearly implies the existence of a nonequilibrium situation within the gas. The relation to the intensity of the background source, further suggests the possibility that this emission may be stimulated at least in part.

In general terms the driving forces capable of sustaining a nonequilibrium situation may be grouped under two major headings:

(a) Chemical reactions behind the shock front that generate a nonequilibrium distribution of concentrations

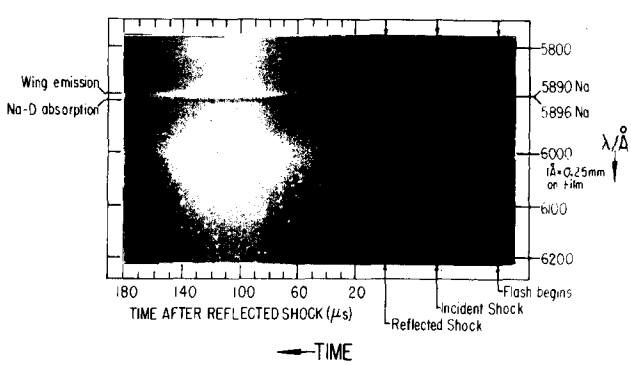

FIG. 1. Time resolved spectrum of the Na *D* line. Sodium was introduced as in trace quantities in an RbI carrier dispersed in argon. Shock conditions were $P_1 = 31$ torr, $P_5 = 9.1$ atm, $T_2 = 3340$ °K, and $T_5 = 7540$ °K.

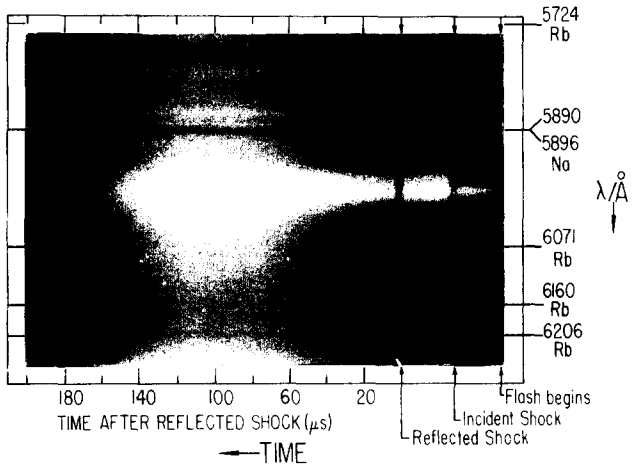

FIG. 2. Time resolved spectrum of Na D and several Rb lines. Shock conditions were $P_1 = 5.1$ torr, $P_5 = 12.0$ atm, $T_2 = 2820\,^\circ$K and $T_5 = 6290\,^\circ$K.

among species or states.

(b) Radiative processes due to temperature differences between the hot gas and its surroundings, which from related degrees of freedom, may produce an energy flow disturbing the distribution of atomic populations. Of course, if energy exchange were the origin of the driving force, there would be some degree of coupling with the chemical process (a).

At first sight the possibility of chemical reaction being responsible for the sustained (ca. 200 μs) emission appears slight. Observations of Berry *et al.* below 4000 °K suggest that reactions of alkali halides should

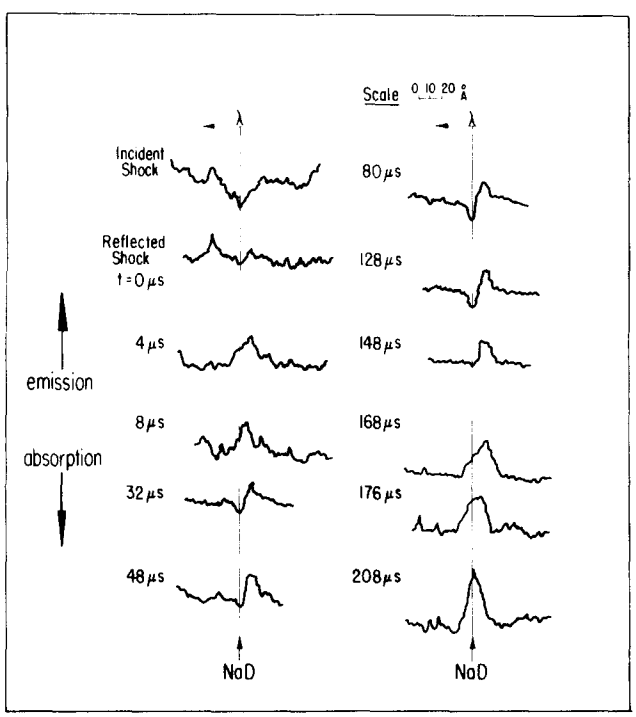

FIG. 3. Densitometer traces of the Na D line taken from Fig. 1. These clearly show the emitting blue wing in the presence of a D line absorption.

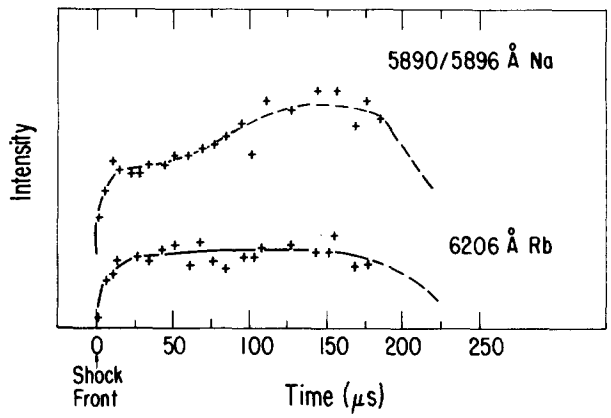

FIG. 4. Variation of the intensities of Na D and Rb 6206 Å radiation with respect to time. Shock conditions are $P_1 = 32$ torr, $P_5 = 9.4$ atm, $T_2 = 3290\,^\circ$K, and $T_5 = 7420\,^\circ$K.

reach equilibrium under our experimental conditions in less than 50 μs. Although the present reaction conditions were somewhat different as regards densities and temperature, we expect that the overall kinetics will not differ greatly from those at lower temperatures.

To look in to this question RbI vapors were shock-heated to the known optimum temperatures of 7000–8000 °K and the emission spectra alone observed. Figure 4 shows the variation with respect to time of the Na D and Rb 6206 Å radiation. Both species show a fall in intensity after about 300 μs; the Na D line displays the additional feature of an initial slow sustained increase for about 200 μs. These effects are quite separate from contact surface compressions, and from the formation of multiple compressions and rarefactions by contact surface–reflected shock front interaction. Such phenomena as these are seen quite clearly at much later times; boundary layer growth with self-reversal of the Na D line is found to occur several hundred microseconds later. The removal of Na from the wall can be discounted because any metal present there would be evaporated in the very hot incident shock. Faizullov *et al.*[2] introduced Na by evaporation from the walls in their line reversal work; although there may be some delay in the evaporation, the salt would be completely taken up by the gas in much less than the 100 μs gas time available in the incident shocks of the present experiments. Furthermore, given the large quantities of Rb used, a similar effect with this metal would be expected. This was not observed, nor were the boundary layer self-reversal problems which affected the work of Faizullov.

At the incident shock temperatures the ionization constants K_p of Rb and Na lie between 4×10^{-5} and 4×10^{-3} and between 4×10^{-11} and 5×10^{-7}, respectively (corresponding to a temperature range of 3000–4000 °K). At equilibrium, with partial pressures of 10^{-3} atm for Rb, and 10^{-6} atm for Na, ionization of 20% and 3%, respectively, will occur at $T_2 = 3500\,^\circ$K. Recall that dwell times and the spectra both imply that this equilibrium is attained.

At the reflected shock temperature of 7500 °K, both

Rb and Na should be amost completely ionized at equilibrium. If ion–atom equilibration were rapid, the absorption spectrum should show a very sharp decrease in metal concentration on passing the reflected shock boundary. Figure 1 shows that for Na at least this is clearly not the case. The work of Haught,[3] Penner,[4] and Boni[5] on the thermal ionization of Cs, Cr, and Ti respectively shows that normal behavior in ionization of these metals involves excitation of the upper electronic levels followed by a relatively slow ionization depletion of the metal concentration. This feature, too, is missing from both our absorption and emission spectra. At 3500 °K almost all (> 90%) of the salt will be dissociated, so that substantial replenishment of metal concentrations from this source is not possible.

Taken together these observations suggest that the metal persists in a state of quasiequilibrium following the reflected shock heating, only relaxing to its final low concentration during or after some 200 μs. In the reflected shock region only the rate processes (1)–(3) need be considered:

$$M^0 + e^- \overset{k_1}{\rightarrow} M^+ + 2e^-; \quad (1)$$

$$X^- + e^- \overset{k_2}{\rightarrow} X^0 + 2e^-; \quad (2)$$

$$M^+ + X^- \overset{k_3}{\rightarrow} M^0 + X^0. \quad (3)$$

where M and X denote metal and halogen, respectively. Sufficient electrons are produced in the incident shock that the rate of any other species as a 3rd body in Reactions (1) and (2) can be neglected. The measurements made by Milstein *et al.*[6] of the low temperature rates of these reactions, indicate that $(k_1/k_2) > 10^2$ at 3500 °K. As the activation energy of Reaction (1) exceeds that of Reaction (2) this ratio may be expected to be larger at higher temperatures. As a result electron loss from X^- will proceed via Reactions (1) and (3) with M^0/M^+ acting as a catalyst. Two extreme cases may be visualized; firstly, that in which $k_1 \gg k_3$. The slow reaction (3) perturbs the equilibrium concentration of M^+ only slightly, so that we expect a rapid partial ionization followed by a slower passage to equilibrium of M^0 and X^- coupled together. This case seems unlikely because of the persistence of M^0 behind the reflected shock. The other extreme has $k_1 \ll k_3$; as a result the metal concentration cannot come to equilibrium immediately—assuming instead a steady state value $[M^0] > [M^0]_{\text{equilibrium}}$. This depletion of the critical species M^+ is analogous to the radiation depletion in argon, observed by Gaydon.[7] A steady state followed by ionization is clearly far more in accord with observation. This model implies a slow fractional disappearance rate of X^- given by $\tau^{-1} \sim k_3 [M^+]$, where $[M^+] \ll [M^+]_{eq}$.

A full quantitative description of the kinetics must await more accurate determination of the high temperature rate constants. At 3500 °K the measurements of Milstein, Ewing, and Berry suggests that $k_3 \sim 10^{-10}$ cm^3 sec^{-1}, whilst $k_1 \sim 10^{-11}$ cm^3 sec^{-1}. However, there are considerable uncertainties associated with the latter rate process in regard to both magnitude and activation energy so that extrapolation to 8000 °K is very hazardous. It is not possible to say with any certainty where the Rb–I system lies between these limits, although the data suggest something closer to the latter than the former.

For Na–I there are additional features of interest due to the existence of an additional ionic–atomic curve crossing, leading to the Na($3p$) state. In this latter case the ionic and atomic limits are close to being isoergic. Under these near-resonant circumstances, Weiner, Peatman, and Berry[8] have shown that the charge exchange cross sections for production of excited states may be "abnormally large" by at least two orders of magnitude. This means that in this case we have strong reason to believe the second model is more appropriate. The rise in the Na concentration as demonstrated by the increased D line emission may be rationalized in terms of the production of Na($3p$) by Reaction (3). As the reaction proceeds and the Na^+ concentration builds up, the rate of production of Na($3p$) may increase, although the total Na concentration falls. It is clear that the evidence points to a chemical disequilibrium, which is intimately associated with low rate of Reaction (2) as compared with that of Reaction (1). (The reasons for this marked difference are discussed in more detail elsewhere.[9])

How this chemical energy in disequilibrium is converted to an atomic population *inversion* is another question altogether. Since the anomalous emission is well of the line centers, alkali–argon interactions suggest themselves. Superficially the Na–Ar system bears some resemblance to the xenon halide molecules in which *laser* action has been obtained by collisional pumping of a bound upper state which decays radiatively to the repulsive lower state.[10] The repulsive lower level $X^2\Sigma_{1/2}$ and the attractive well connected to the $3p$ Na level ($A^2\Pi_{1/2,3/2}$) are well characterized in Na–noble gas interactions.[11] However, the attractive upper Π state is associated with the formation of red satellites; the blue wings in which we are more interested are assigned to a $B^2\Sigma_{1/2}$ term, generally presumed to be repulsive. The latter arises only from the $^2P_{3/2}$ term; the $^2P_{1/2}$ term gives rise only to the attractive $^2\Pi_{1/2}$. (It must be added that the attractive excited states can, in principle, give blue as well as red wings. Our limited resolving power may be responsible for the failure to observe a $^2P_{1/2} \rightarrow {}^2S_{1/2}$ blue wing.)

The situation for the higher states of Rb–noble gas interactions is considerably more complex. The calculations of Pascale and Vandeplanque[11] extend only to 4^2F for Rb–Kr, so that the following discussion depends on analogies with Cs potentials. The Rb transitions for which data have been obtained are

$6^2D_{5/2} \rightarrow 5^2P_{3/2}$ at 6298 Å,

$6^2D_{3/2} \rightarrow 5^2P_{1/2}$ at 6206 Å,

$8^2S_{1/2} \rightarrow 5^2P_{1/2}$ and $5^2P_{3/2}$ at 6160 and 6071 Å,

for which we observe blue wings in emission, and

$7^2D_{5/2} \rightarrow 5^2P_{3/2}$ at 5725 Å,

for which we do not.

The analogous levels 6^2P, 7^2D, 9^2S have been calculated for Cs–Xe interaction in Ref. 11. The 9^2S ex-

hibits a potential well of depth 700 cm^{-1} whilst the ground state $6\,^2P$ has wells of only 500 cm^{-1} depth. Clearly blue shifts cannot result from these interactions, unless it be by radiation from a region up the repulsive wall. We note that the blue wing emissions we observe lie closer to the main line than do the true satellite bands.

Kielkopf[12] has analyzed satellite band positions in terms of the coefficient C_{12} of the repulsive potential term $C_{12}r^{-12}$, and has found that C_{12} increases with the excitation of the alkali atom. In other words, the higher states have steeper repulsive walls so that blue shifts from this region are possible.

Tsongas and Koutsoyannis have rationalized the strong increase of C_{12} with increasing atomic excitation in terms of the greater effective radius of the *alkali* atom.[13] Thus, C_{12} should be independent of the inert gas, as is found experimentally. Extending this very tentatively to M–X interactions, and assuming that the ion–ion curve is more strongly repulsive than the atomic curves due to the inert gas structures of the ions, it can be seen that the energy of any crossing on the repulsive wall will increase with the size of C_{12}.

Kielkopf's data shows that crossings of the atomic states with the ionic potential wall will be thermally inaccessible. However, as the repulsive curves are nearly parallel, curve crossings are not required for state changes and the energy necessary for transfer between atomic and ionic states will be substantially below that to reach the actual crossing point. Collision durations at velocities of 10^5 cm/sec are typically 10^{-13} sec, whereas the radiative lifetime of free Na and Rb states is in the region of 10^{-8} sec, which suggests that the M–X complex will usually dissociate before radiation can occur. However, the atomic lifetime in the presence of a halogen and a dense atmosphere of inert neighbors may be very different from that of the free atom, due in part to the extra factor of radiationless transitions, i.e., collisional stabilization. Conceivably, background radiation might induce stimulated recombination—which would rationalize the strength of the wing emission in the presence of the background radiation, which contrasts sharply with its very low intensity in the absence of background radiation.

Mechanisms for the anomalous wing emissions can clearly be given on the basis of an X^- disequilibrium, which is the interpretation we favor. However, the lack of reliable estimates of the cross sections involved makes it somewhat premature to enter discussion more detailed than that given earlier in this section.

Energy exchange mechanisms for producing population inversions by temperature differentials may be discussed under three headings:

(i) Heat loss to shock tube walls.

(ii) Radiative loss to the cold exterior, in which category the cooler unshocked gases are included.

(iii) Radiative gain from the high temperature flash lamp.

We belive none of these is responsible for the observed emission, for the following reasons. Heat loss to the walls may be dismissed on the grounds that it will effect only a small region of the gas, and would be characterized by reversal of the Na *D* line. Line reversal, characteristic of cool wall zones, is observed but only at much later times. Loss by radiation is known to deplete the population of the radiating level; this perturbation of the equilibrium might then be made up by $X^- + M^+ \rightarrow M^0 + X^0$ providing a repopulation of the upper level. The mechanism to produce the blue wings is identical with that resulting from chemical disequilibrium.

Given that the blue wing is strong only in the presence of a strong background radiation it might be surmised that the energy of the flash lamp plays a critical kinetic role. However, the intensity of the Na wing does not appear to depend upon the strength of the *D* line absorption, so the mechanism responsible for the blue wing emission apparently does not depend on Na atoms in their ground state.

Finally, consideration is given to possible rationalizations of the wing emission phenomenon which do not involve an atomic inversion. Consider a line broadened by self-absorption (i.e., an optically thick system exists); if the emissivities of lamp and gas are comparable then the combined effect of a broadened emission line and a normal absorption line may be to produce emitting wings adjacent to a central absorption line. Against this explanation we cite the following items of evidence:

(a) Although the asymmetry of the Na emission could be explained on the basis of overlap with the weaker "red" part of the doublet, this will not serve to explain the structure of the single Rb lines.

(b) There exists no correlation with the strength of the emission which persists after the flash lamp emission has faded. In particular the Rb lines have very much lower oscillator strength than the Na *D* line, yet show strong emission. The 5725 Å line which is stronger than the 6170 Å line shows no wing emission.

(c) Observed line shapes in the post lamp region show no unusual blue wing broadening.

The final question remains; is the system showing actual gain, or is there only a spontaneous fluorescence in the blue wing? Gain has been proposed for such systems under other conditions.[14] Measurements of coherence, beam divergence, etc., have not been made yet. However, measurements have shown that the intensity of the Na wing emission in certain shocks is proportional to the lamp intensity in the same wavelength region, as the latter changes by a factor of about 2. This indicates that the system possesses a negative optical density at this wavelength (~ 5880 Å). Moreover, one can get an idea of the intensity of this emission from spectra recorded with two layers of film; the intense blue wing emission of the Na *D* penetrated the upper film, including the antihalation coating, and gave an image of intermediate optical density on the lower film. Hence we infer that it is likely that the system is superradiant in the blue wings of the Na *D* line and perhaps in the corresponding wings of four lines of Rb as well.

ACKNOWLEDGMENT

This work was supported by a grant from the Army Research Office—Durham.

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