

## Inverted Population in Dissociation of CsBr Molecules

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The dissociation of diatomic CsBr molecules in a shock wave has been studied by time-resolved absorption spectroscopy. Absorption by neutral cesium atoms increases monotonically toward its equilibrium value as dissociation proceeds, but under a wide range of conditions, absorption by Br<sup>-</sup> ions goes rapidly to a maximum and then falls to its equilibrium value. The results show that under some conditions, the principal primary products of dissociation are ions, rather than atoms or a thermally equilibrated mixture of atoms and ions.

### I. INTRODUCTION

This report is a study of the primary dissociation process in the collisional dissociation of "ionic" diatomic molecules. The experiments discussed below show that the primary step in the shock-initiated thermal dissociation of CsBr molecules in argon proceeds neither to the dissociated neutral atoms in their ground states, nor to the thermal equilibrium distribution of dissociated atoms and ions, but to an inverted distribution of dissociated species. Under a wide range of easily achieved conditions, the primary dissociation products are predominantly the separated ions, Cs<sup>+</sup> and Br<sup>-</sup>. The highly inverted distribution then relaxes slowly to the equilibrium distribution of dissociation products: atoms, ions, and electrons.<sup>1</sup>

This report describes the basic physical phenomenon in terms of the states involved, the apparatus and measuring techniques, and some of the inferences that can be drawn from the measurements of the range of variation of the population inversion or overshoot, its dependence on temperature and pressure, and the time scales of dissociation and relaxation. We shall remark on the relaxation mechanism but shall make no attempt to elucidate it here.

The alkali halides are the classic examples of molecules in which the noncrossing rule is violated. The "zero-order" internuclear potential for the pure neutral atomic states can be approximated as a straight horizontal line at large internuclear distances  $R$  while the corresponding potential for the pure ionic states can be represented by a Coulomb curve. The asymptote of the curve originating at the separated atom limit, with atoms in their ground states, is always lower in energy than that of the separated ions, because the ionization potential of the alkali,  $I(M)$ , is always larger than the electron affinity of the halogen,  $A(X)$ . This is indicated in Fig. 1. The dissociated ions are closed-shell species and generate a  $^1\Sigma^+$  state of the molecule; the atoms in their ground states ( $^2S$  for  $M$ ,  $^2P_{3/2}$  for  $X$ ) also generate

a  $^1\Sigma^+$  state. In general, states corresponding to any other dissociation limits between  $[M(^2S) + X(^2P_{3/2})]$  and  $[M^+(^1S) + X^-(^1S)]$  also generate  $^1\Sigma^+$  states, but these need not concern us explicitly. If the Born-Oppenheimer approximation were valid, the noncrossing rule would predict that, as  $R$  decreases, the upper molecular state changes its character from ionic to atomic while the lower state changes from atomic to ionic. The change should occur very close to the crossing distance  $R_x$ , defined by the condition  $e^2R_x^{-1} = I(M) - A(X)$ .

Because  $I(M) - A(X)$  is relatively small for the alkali halides,  $R_x$  is relatively large, so the overlap of the alkali valence  $s$  orbital with the halide valence  $p\sigma$  orbital is small when  $R = R_x$ . This, in turn, means that the probability is small for charge transfer when  $R = R_x$ , and that the probability of the molecule's obeying the noncrossing rule is small. For CsBr,  $R_x = 51.5$  a.u.; this is a clear case for which the potential curves are best considered as crossing, rather than as obeying the adiabatic noncrossing rule. One can estimate the probability of crossing by computing the approximate off-diagonal element of the nuclear kinetic energy operator, but that calculation does not pertain directly to the problem at hand.<sup>2</sup>

In several of the alkali halide ultraviolet spectra, one sees strong continuous absorption indicating that the upper state photodissociates, even when the energy of upper state is below the dissociation limit of the separated ions. This implies that the upper state does violate the noncrossing rule. Potassium iodide is one such example. In only two cases, LiI and NaI, those molecules with the smallest values of  $R_x$ , is there spectral evidence for binding in the upper state<sup>3</sup>; the binding arises from the attractive Coulomb forces of the adiabatic curve of the excited  $^1\Sigma^+$  state for  $R = R_x$ . The potential curve diagram for CsBr shown in Fig. 1 illustrates this phenomenon. The lower curve is a Coulomb-plus-exponential; the upper state is based on the spectroscopic work of Davidovits and Brodhead.<sup>4</sup>

<sup>1</sup> The first report, a demonstration of the existence of the phenomenon, was given at the Sixth International Shock Tube Symposium, Freiburg, April, 1967, and has been submitted as part of the proceedings of this symposium. These are scheduled for publication in *Physics of Fluids* in 1968.

<sup>2</sup> R. S. Berry, *J. Chem. Phys.* **27**, 1288 (1957) and Refs. therein.

<sup>3</sup> H. Levi, Doctoral dissertation, Berlin, 1934; H. D. Schmitt-Ott, *Z. Physik* **69**, 724 (1931).

<sup>4</sup> P. Davidovits and D. C. Brodhead, *J. Chem. Phys.* **46**, 2968 (1967).

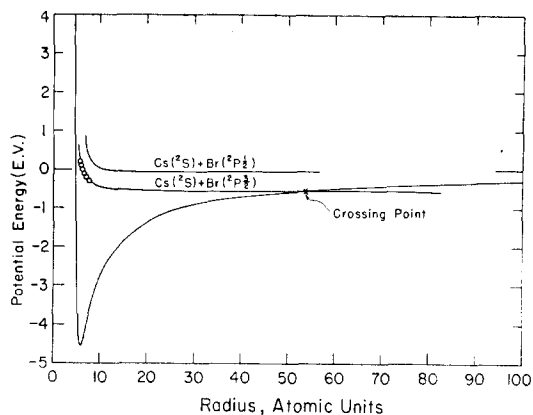


FIG. 1. Potential curves for CsBr, showing the attractive ionic state, the first two repulsive atomic states, and the crossing point.

The question naturally arises as to what happens when an alkali halide molecule in its ground electronic state dissociates as a result of simple collisions. If the molecule follows the ionic curve rather than the adiabatic curve defined by the noncrossing rule, then the primary dissociation products in a hot alkali halide system would be ions and not atoms. This will be the case if charge-transfer probability is small. Naturally, such ions would represent a system far from equilibrium; the normal ratio of dissociated ion pairs to dissociated  $\alpha$  to  $n$  pairs is of order 1:10, due primarily to the 12-fold degeneracy of  $M(^2S) + X(^2P_{1/2,3/2})$ . We have undertaken an experimental investigation of the shock-wave initiated thermal dissociation of alkali halides. The study began with CsBr in order to search for the existence of such a disequilibrium and study its magnitude and its relationship to the manner in which collisions produce dissociation.

## II. EXPERIMENTAL METHOD

The apparatus is a modification of a shock tube used in previous investigations involving alkali halides.<sup>5</sup> The final (downstream)  $3\frac{1}{2}$  ft of the tube are stainless steel. The inside crosssection is  $3\frac{1}{2} \times 3\frac{1}{2}$  in. The entire driven section is 15 ft long. Approximately 2 in. from the downstream end of the tube, a plug is threaded in the tube wall; the plug supports a nichrome filament a proximately flush with the tube wall. For these experiments, the driver gas was helium; the driven gas, generally argon, and in a few cases, nitrogen. Driving pressures were of order 100 psi; driven gas pressures  $P_0$  were of order 50 torr.

The salt was introduced by placing a small (5–10 mg) amount of CsBr in aqueous solution on the nichrome filament; the filament was warmed to evaporate the water and fuse the salt to the filament. The tube was

filled with the desired amount of argon and the rest of the apparatus was made ready. The filament was then heated strongly to vaporize the salt, which immediately became a fine smoke dispersed in the carrier gas. Mixing of the smoke in the argon was achieved by convection. After the filament current was turned off and the filament cooled, the shock wave was released. The amount of salt represented about 0.1 mole % of the carrier gas. This concentration could only be estimated by evaporating salt into the carrier gas and then measuring the volume over which the salt was distributed in the absence of a shock.

Because of the thermodynamic parameters of the alkali halides, it was possible to conduct the experiments in an extremely simple way. The conditions of shock were chosen so that the incident shock would only vaporize the smoke particles to produce a vapor of undissociated diatomic molecules. For this reason the incident shock-wave temperatures  $T_1$  were kept in the range 1200°–2000°K. Thus the incident shock merely prepared the sample. Then the *reflected* shock raised the temperature quickly to a value at which a significant fraction (10%–99+%) of the salt would be dissociated at equilibrium.

The salt particles produced from the hot filament were small enough (0.1  $\mu$ diam) to evaporate completely behind the incident shock front in a time well under 1  $\mu$ sec. This evaporation time is a conservative estimate based on the Langmuir equation for pure diffusive evaporation<sup>6</sup>; the validity of this equation was demonstrated by Whitmore and Moser for NaCl spheres in argon.<sup>7</sup> The average time that the molecules observed in the reflected shock had spent in the incident shock was 15  $\mu$ sec. It is therefore entirely reasonable to assume that the observed gas in the incident shock came to thermal equilibrium before it encountered the reflected shock.

The effect of the salt on the gas temperature was small because of its low concentration. Typically, a shock which in pure argon would give a reflected shock temperature of 3472°K, would give a temperature of

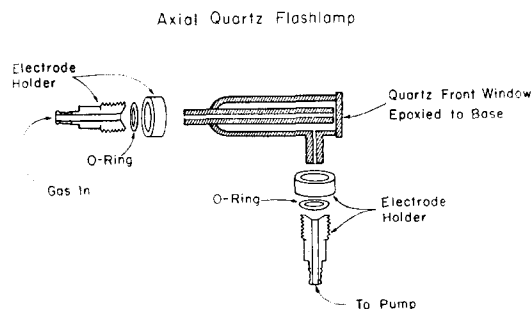


FIG. 2. The spectral flash lamp.

<sup>5</sup> (a) R. S. Berry and C. W. Reimann, *J. Chem. Phys.* **38**, 1540 (1963); (b) R. S. Berry, C. W. Reimann, and G. N. Spokes, *ibid.* **37**, 2278 (1962).

<sup>6</sup> I. Langmuir, *Phys. Rev.* **12**, 368 (1918).

<sup>7</sup> D. H. Whitmore and J. B. Moser, *J. Chem. Phys.* **33**, 917 (1960).

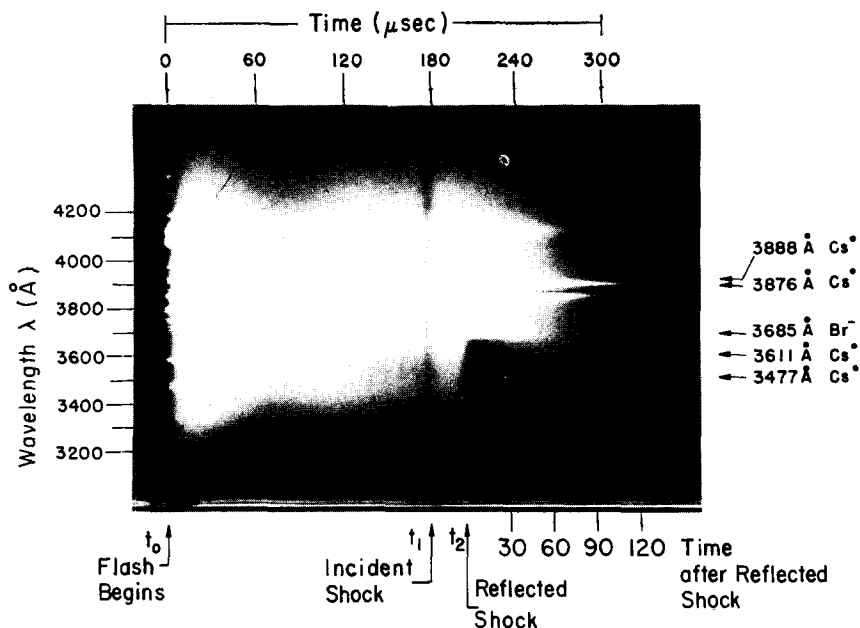


FIG. 3. A typical time-resolved absorption spectrum for CsBr in Ar. At  $t_0$ , the flash is set off; at  $t_1$ , the incident shock passes the observation point; at  $t_2$ , the reflected shock passes the observation point, 16 mm from the end wall.

3290°K if CsBr were present under our conditions and if the CsBr were merely to vaporize to diatomic molecules. Thus 3290°K would presumably be the kinetic-rotational-vibrational temperature in the reflected shock before dissociation. After full equilibrium is attained, the same reflected shock would have a temperature of 3146°K.

The monitoring was straightforward. The species of interest are  $\text{Cs}^0$ ,  $\text{Br}^0$ ,  $\text{Cs}^+$ ,  $\text{Br}^-$  and electrons. It is sufficient to monitor one neutral and one ion concentration to obtain conclusive evidence regarding the existence and magnitude of an overshoot. The absorption spectra of  $\text{Cs}^0$  and  $\text{Br}^-$  were the obvious choices for time-dependent monitoring. The principal series lines of Cs and the photodetachment continuum of  $\text{Br}^-$  are both sufficiently well characterized to be completely unambiguous (the latter because of its sharp threshold)<sup>8</sup> and both are sufficiently intense to be seen even when the absorbers are present in small concentration.

A small capillary flash, viewed "end on," provided the background for the spectra. A sketch of the lamp is shown in Fig. 2. The lamp was supplied with power from a 74- $\mu\text{F}$  bank of capacitors, charged to approximately 6.3 kV. Inductors in transmission line coupling with the capacitors extended the life of the flash to 200  $\mu\text{sec}$  or more; for the last 175  $\mu\text{sec}$ , the light intensity was essentially constant. The lamp was triggered by a delayed signal from a thermal resistance gauge upstream from the observation region. The discharge was initiated about 50  $\mu\text{sec}$  before the incident shock passed the point of observation.

The light from the lamp traversed the tube four times before entering a rotating-drum spectrograph (which was described previously).<sup>8</sup> The folded light path defined

a thin slab ( $\sim 1$  mm at widest point) perpendicular to the tube axis. No time resolution was lost in the multiple pass system. The spectrograph slit was 50  $\mu$  high and 25  $\mu$  wide; the camera drum, 9 in. diam, rotated at 10 000 rpm, corresponding to 250  $\mu/\mu\text{sec}$ . The time resolution of the system was about 1  $\mu\text{sec}$ .

Spectra were recorded on Kodak 103-0 film, developed in D-19 developer. The film was calibrated under the same conditions as those used for obtaining spectra. The cesium line used for the quantitative interpretation in the following section was the 6s-8p doublet at 3875, near but at longer wavelength than the bromide photodetachment threshold at 3685 Å. Other cesium lines showed the same behavior as this one, but were less convenient because of their intensities, or in some cases, because they were above the  $\text{Br}^-$  threshold. The quantitative data for  $\text{Br}^-$  were based on measurements at 3637 Å, because this is a wavelength well away from interferences. Other clear wavelength regions showed the same behavior for  $\text{Br}^-$ .

In addition to the  $\lambda$ - $t$  photographs, a few  $x$ - $t$  photographs were taken of total emission and in the case of NaI, of light from the NaD line. The  $x$ - $t$  photographs covered the region from the end wall to a point approximately 4 cm away.

Films of the  $\lambda$ - $t$  spectra were scanned with a Jarrell-Ash microdensitometer at intervals of 0.5 mm, corresponding to 2  $\mu\text{sec}$ , up to times of about 12  $\mu\text{sec}$  after  $t_2$ , the time of passage of the reflected shock, and at time intervals of 4  $\mu\text{sec}$  thereafter.

### III. EXPERIMENTAL RESULTS

A typical time-resolved spectrum is shown in Fig. 3. With very small salt concentrations, it has proved possible to obtain spectra of quality as high as in

<sup>8</sup> R. S. Berry, J. C. Mackie, R. L. Taylor, and R. Lynch, *J. Chem. Phys.* **43**, 3067 (1965).

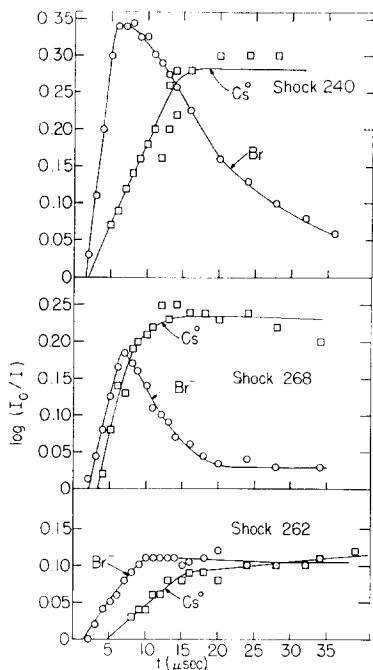


FIG. 4. Typical curves for absorption vs time for  $\text{Cs}^0$  and  $\text{Br}^-$  in shocks of various temperatures. Quoted temperatures are the equilibrium values for a reflected shock in pure argon; actual values are approximately  $175^\circ$ – $200^\circ$  lower. Shock 240:  $4500^\circ\text{K}$ ; Shock 268:  $3680^\circ\text{K}$ ; Shock 262:  $2400^\circ\text{K}$ .

conventional fast-flash spectra. At time  $t_0$ , one can see the onset of continuous emission from the lamp, followed by a period preceding the passage of the incident shock; then, in essence, the experiment begins at  $t=t_1$ . The dark line at  $t_1$  is due to the increased scattering by dust compressed by the incident shock; it affords a useful check on the time of passage of the incident shock. The time  $t_2$ , when the reflected shock reaches the observation window, is marked by the sudden onset of absorption by the halide ion. The sharp threshold at  $3685 \text{ \AA}$  is, in a sense, a more unique fingerprint of  $\text{Br}^-$  than an absorption line would be, insofar as impurities could give rise to nearby interfering lines, whereas the photodetachment continuum is a most unambiguous feature in the spectrum.

When the reflected shock passes the observation point, the intensity of the continuous halide absorption rises rapidly to a maximum, and then falls in intensity, slowly, to a steady value, presumably the thermal equilibrium value in the reflected shock. The atomic cesium lines show no such overshoot; rather, the cesium line absorption increases monotonically and approaches a steady value in about the same time that the halide continuum absorption decreases from its maximum to its steady intensity. The atomic cesium lines reach detectable intensity about  $4 \mu\text{sec}$  after the first appearance of  $\text{Br}^-$  and never before the  $\text{Br}^-$  appears. Figure 4 shows some typical plots of the intensities of halide and neutral cesium absorption as functions of time.

The amount of halide overshoot is a function of the temperature in the reflected shock. Below  $2700^\circ\text{K}$ , no maximum could be observed. The magnitude of the overshoot increased with temperature to the highest temperatures studied,  $\sim 4700^\circ\text{K}$ , as shown in Fig. 5. (At higher temperatures, the incident shock produces dissociation.) No simple functional relationship was found between the magnitude of the overshoot and the temperature. Nevertheless the increase in overshoot with temperature, over the range  $2700^\circ$ – $4700^\circ\text{K}$ , is a clear demonstration that the overshoot is truly a characteristic of the bulk gas and is not a boundary layer phenomenon.<sup>9</sup>

The interval between  $t_2$  and the time of maximum halide absorption is also a function of temperature. At the lowest temperatures of interest, this interval is about  $6 \mu\text{sec}$ ; at the highest temperature, it is about  $2 \mu\text{sec}$ , slightly longer than our time resolution. The experimental time resolution is sufficient to give about 3–5 points on the rising (early) side of the halide curves. This is enough to define the rising curve, but we cannot differentiate meaningfully between a linear increase of the halide concentration and any more complicated time dependence. At the lower temperatures, the duration of the period of maximum absorption is significantly longer than our resolving time, sometimes as long as  $6 \mu\text{sec}$ . At higher temperatures, this interval drops to  $\sim 2 \mu\text{sec}$  or less.

The  $1/e$  time for relaxation of the halide overshoot and for the rise of  $\text{Cs}^0$  absorption is about  $5$ – $10 \mu\text{sec}$ ; the relaxation rate increases with temperature. Figure 6 shows some typical first-order plots for the  $\text{Br}^-$  concentration at various temperatures. At temperatures below  $3500^\circ\text{K}$ , where the overshoots are small, one cannot get such clear first-order behavior. The alkali concentration rises monotonically to a steady value. Although the scatter in the alkali data is greater than in the halide data, it is clear that the rate of rise of alkali absorption is much closer to the rate of halide

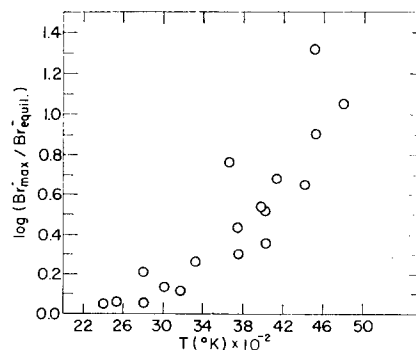


FIG. 5. Temperature dependence of excess  $\text{Br}^-$  concentration.

<sup>9</sup> S. Byron and N. Rott, Proc. Heat Transfer Fluid Mech. Inst. 1961, 38.

relaxation than to the rate of appearance of halide. The scatter may be due to the time variation of the alkali line shape (from ionic Stark broadening) or from interference from the nearby silicon lines.

That the relaxation appears to be first-order with respect to halide concentration is by no means an elucidation of its mechanism. In fact one line of Fig. 6, that marked with circles, appears to show more than one mechanism of relaxation. The line marked with squares and the "circle" curve were derived from data taken at similar temperatures, yet the "circle" curve seems to be governed by the same rate constant as the "square" curve only at late times. It is plausible that more than one relaxation mechanism could be involved, as we discuss in the final section. Shocks were carried out with (reflected shock) pressures of Ar from 2–15 atm. Over this range, no significant variation in  $\text{Br}^-$  or  $\text{Cs}^0$  absorption could be found, either in rate or amount, as a function of argon concentration. This signifies two things. At early times behind the reflected shock, when the principal process occurring is dissociation, the lack of significant dependence on pressure means only that the curve of bromide absorption intensity rises too steeply for our time resolution to show more than a generally rising shape. The lack of pressure dependence in the cesium absorption curve, or in the halide curve at late times, does indicate that argon is either unimportant to the relaxation mechanism or that its concentration is so high that the rate is not sensitive to the argon density in much the same way that "unimolecular" reactions exhibit first-order kinetics at high densities.

The results of the  $x-t$  photographs warrant some mention. An example is shown in Fig. 7. The incident shock front is just barely visible in the original photograph. The reflected shock front is clearly visible, largely because of emission of alkali principal series lines. The most distinctive features of the  $x-t$  photograph is the dark zone between the end wall and a point 1–1.5 cm away, and between the time of passage of the reflected shock and a time of about  $50 \mu\text{sec}$  later, at longest. We have so far been unable to detect any overshoot in

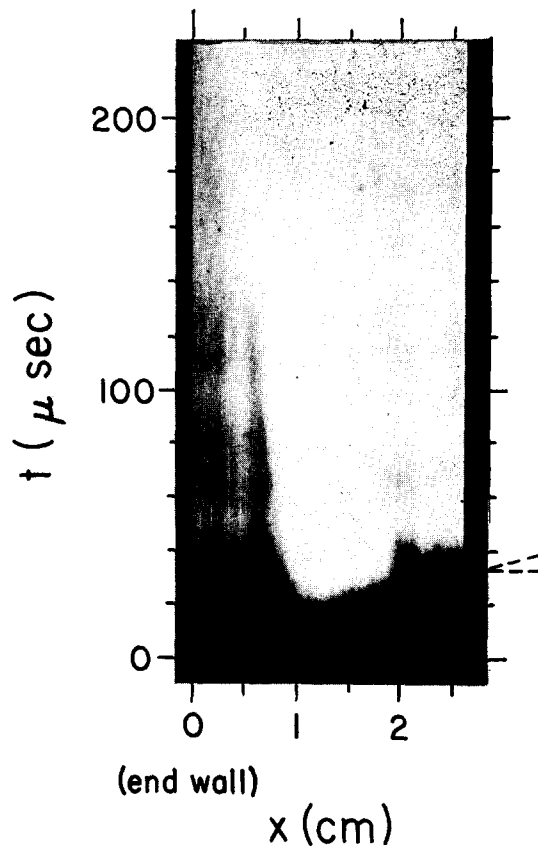
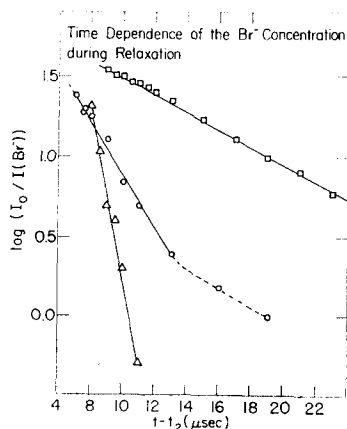


Fig. 7. A typical  $x-t$  photograph of total emission from a shock in  $\text{NaI}+\text{Ar}$ ;  $x-t$  photographs taken with filter interposed to pass only the  $\text{NaD}$  line are indistinguishable from those taken without a filter. The small triangle at right was drawn from the original photograph, to indicate the slope of the reflected shock front. The leading edge of this front may be lost in reproduction. The weak emission behind the reflected shock after about  $20 \mu\text{sec}$  is presumably due to the boundary layer, and should not be confused with the strong emission from the bulk gas which first appears about 1 cm from the end wall and at  $t \geq 20 \mu\text{sec}$ . (Photograph taken on Plus-X film.)

FIG. 6. The time dependence of  $\text{Br}^-$  concentration for shocks at various temperatures. Intensities were recorded at  $\lambda = 3637 \text{ \AA}$ . (Shock 240)  $\square$ :  $4500^\circ\text{K}$ ; (Shock 257)  $\circ$ :  $4440^\circ\text{K}$ ; (Shock 242)  $\triangle$ :  $5360^\circ\text{K}$ .



regions not showing the "dark space" in  $x-t$  photographs; where there is a dark zone in the  $x-t$  photograph there is an overshoot in the  $\lambda-t$  photograph, and the rate of disappearance of the dark zone coincides as well as we can tell, with the time for relaxation of the ions following the overshoot. We infer that the dark zone with no excited alkali emission probably coincides with the region of overshoot, in which the neutral alkali-atom population is low. The length of the dark zone corresponds, so far as we can ascertain, to the extent of the region containing shocked salt. In other words, the length of the dark zone is approximately the length of the region over which salt smoke can be found if no shock wave is released, multiplied by the ratio of the initial density to the reflected-shock density. We have not determined whether the intense emission following and to the right of the dark zone is due to alkali metal in the bulk gas or the boundary layer. The weak emission appearing near the end wall between 10 and

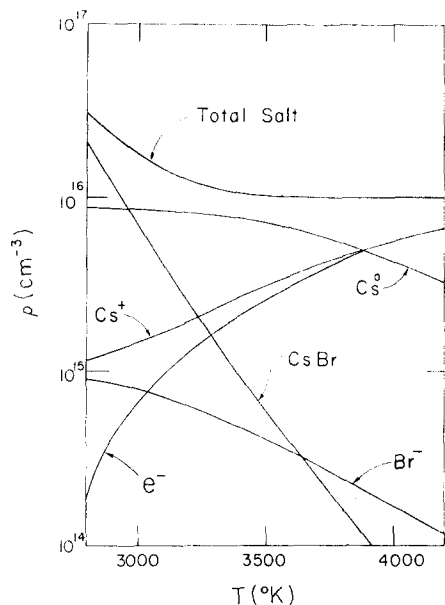


FIG. 8. Temperature dependence of equilibrium concentrations of  $\text{Cs}^0$ ,  $\text{Cs}^+$ ,  $\text{Br}^-$ ,  $e^-$ ,  $\text{CsBr}$ , and total salt concentration. Concentration of dissociated molecules is fixed at  $10^{16} \text{ cm}^{-3}$ . The concentration of  $\text{Br}^0$  varies between  $9.1 \times 10^{16}$  and  $9.9 \times 10^{16}$  over the temperature range shown in this figure.

20  $\mu\text{sec}$  after  $t=0$  is probably due to the boundary layer, but we have not yet made any specific attempt to locate its origin. Traces taken with a narrow-band filter passing only the most intense alkali resonance line gave streak pictures indistinguishable from those taken with no filter. We infer that essentially all the emitted light does come from the alkali atoms in their first excited  $P$  states.

#### IV. INTERPRETATION

The principal interpretation of the data seems unambiguous. The primary dissociation process for  $\text{CsBr} + \text{Ar}$  leads to a significant overpopulation of the ionic dissociation limit, with  $\text{Cs}^+$  and  $\text{Br}^-$  the principal species present instead of  $\text{Cs}^0(^2S)$  and  $\text{Br}^0(^2P_{3/2})$ , the dissociation products in their ground state. At the highest temperatures, the ratio of the maximum intensity of halide absorption to its equilibrium value provides an immediate demonstration that the primary dissociation products of  $\text{CsBr}$  are  $\text{Cs}^+$  and  $\text{Br}^-$ . The maximum concentrations are an order of magnitude greater than the equilibrium values. One can see from Fig. 8, the equilibrium concentrations of components in the gas at various temperatures, that the halide concentration is about an order of magnitude less than the total halogen concentration. (The halogen occurs solely as atoms and negative ions in our range of temperature density.)

At lower temperatures, no maximum in  $\text{Br}^-$  concentration appears. Nevertheless our results show no indication that any neutrals are generated as primary

dissociation products. We see this by examining the quantity

$$\vartheta = \frac{[\text{Br}^-(t)]/[\text{Br}^-]_{eq}}{[\text{Cs}^0(t)]/[\text{Cs}^0]_{eq}}$$

At equilibrium,  $\vartheta = 1$ ; if there were no electrons, or at early times when we can disregard the small number of electrons, and if we make an assumption that the system can be treated as though it were passing adiabatically through a sequence of almost stationary states, then we could define a time-dependent free energy function  $\Delta F(t) = RT \ln(\vartheta^2)$ . If the primary products of dissociation were to include some neutrals as well as ions, then  $\vartheta(t)$  would approach a finite value as  $t$  approaches 0. If ions were the only product,  $\vartheta^{-1}(t) \rightarrow 0$  as  $t \rightarrow 0$ . In all of our shocks,  $\vartheta^{-1}$  is zero in the sense that we can detect no neutral alkali atoms, for at least 2  $\mu\text{sec}$  after the reflected shock passes. This means that either we do not have the resolution or sensitivity to detect small alkali concentrations, or the primary dissociation products are ions in all the shocks we have studied.

The reason for the overshoot or population inversion clearly lies in the inefficiency of electron transfer from  $\text{Br}^-$  to  $\text{Cs}^+$  at energies at or above the energy of the  $\text{Cs}^0 + \text{Br}^0$  ground state. Let us take  $E=0$  as the energy of  $\text{Cs}^0(^2S) + \text{Br}^0(^2P_{3/2})$ , and suppose that there is a probability amplitude  $P(E)dE$  for a bound  $\text{Cs}^+ - \text{Br}^-$  pair to become a free  $\text{Cs}^0 - \text{Br}^0$  pair with kinetic energy in the range  $dE$  around  $E$ . The collisional vibrational excitation process  $\text{CsBr} + \text{Ar} \rightarrow \text{CsBr}^+ + \text{Ar}$  must simply excite each vibrationally excited molecule out of every region  $dE$  with a probability much greater than  $P(E)dE$ , and get the molecule up to the ionic dissociation limit  $E_I = \text{I.P.}(\text{Cs}) - \text{E.A.}(\text{Br}) = 3.86 - 3.36 = 0.5 \text{ eV}$ , with a total probability much greater than

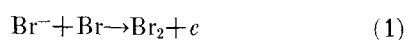
$$\int_0^{E_I} P(E)dE.$$

By varying the alkali halide, and thereby varying the crossing distance  $R_x$  and the energy at which the Coulomb and atomic curves cross, it may be possible to find examples for which  $\vartheta^{-1}(0) \neq 0$  and thereby to study the dissociation process itself. One now has theoretical means to find approximate forms for  $P(E)$  with reasonable atomic wavefunctions, and go beyond approximations like the Landau-Zener approximation as applied to alkali-halogen interactions.<sup>16</sup> If one can unambiguously distinguish dissociation to atoms from relaxation of ions to atoms, thereby determining the branching ratio for dissociation into the two channels, one has a probe for determining the amount of time a dissociating molecule spends in its very highly excited vibrational states, on its way to dissociation.

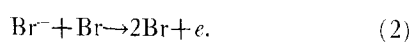
One of the most prominent problems raised by the

<sup>16</sup> J. L. Magee, *J. Chem. Phys.* **8**, 687 (1940); see also Ref. 1.

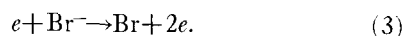
existence of the overpopulation of the ionic dissociation channel is that of finding the mechanism of the relaxation process. The mechanism is probably not simple direct electron transfer from  $\text{Br}^-$  to the empty  $6s$  orbital of  $\text{Cs}^+$ ; if this were an efficient process, there would be no overshoot. Transfer to excited orbitals of cesium is energetically impossible unless large amounts of nuclear kinetic energy are transferred to electronic energy; we assume this process is improbable. The lack of significant pressure dependence of the relaxation rate suggests that the argon does not play an important role in the relaxation. We have not yet studied the dependence of the relaxation rate on cesium and bromine concentration by themselves, and can only mention here the most likely mechanisms. One of the most probable pathways for releasing electrons from the  $\text{Br}^-$  ions is by associative detachment and the closely related collisional detachment. It was shown first by Bates and Massey<sup>11</sup> that processes like



may have quite large cross sections. Under the conditions of our experiments, pure collisional detachment is energetically possible, i.e.,



Process (2) is essentially the same as (1), differing only insofar as the product atoms are in a state of the vibrational continuum, rather than in a bound vibrational state. Thus in our system, (2) can be expected to play a very important role if (1) does. A second relaxation mechanism which might be important is collisional detachment by electron impact,



This process, with  $\text{H}^-$  instead of  $\text{Br}^-$  has been investigated experimentally at energies down to about 20 eV by Rundel, Harrison, and Dance<sup>12</sup> and theoretically at lower energies as well.<sup>13</sup> The experiments and theory agree quite well, and suggest that the cross section for Process (3) decreases rapidly toward zero as the energy falls. However, the experiments do not yet reach into our thermal region, and more important, the theoretical treatment makes no allowance for the polarization of the halide by the incoming electron. The importance of the attractive polarization interaction in  $e\text{-H}^-$  scattering

<sup>11</sup> D. R. Bates and H. S. W. Massey, *Phil. Mag.* **45**, 111 (1954); see also J. N. Bardsley, *Proc. Phys. Soc. (London)* **91**, 300 (1967) and A. Herzenberg, *Phys. Rev.* **160**, 80 (1967) for recent results and references.

<sup>12</sup> D. F. Dance, M. F. A. Harrison, and R. D. Rundel, *Proc. Roy. Soc. (London)* **A299**, 525 (1967); R. D. Rundel, M. F. A. Harrison, and D. F. Dance, *Proc. Intern. Conf. Phys. Elec. At. Collisions*, 6th, Leningrad, July, 1967, 36 (1967); see also G. Tisone and L. M. Branscomb, *Phys. Rev. Letters* **17**, 236 (1966) for higher-energy measurements.

<sup>13</sup> M. R. C. McDowell and J. H. Williamson, *Phys. Letters* **4**, 159 (1967); M. R. H. Rudge, *Proc. Phys. Soc. (London)* **83**, 1 (1964).

has been pointed out by McDowell.<sup>14</sup> For  $e\text{-Br}^-$  interaction, with a polarizability of about  $4 \text{ \AA}^3$  for  $\text{Br}^-$ ,<sup>15</sup> the interaction energy of a point electron and a  $\text{Br}^-$  ion is a maximum of 5 eV at  $r=3 \text{ \AA}$  and becomes zero at 1.26  $\text{ \AA}$ . This suggests the possibility that the cross section for Process (3) rises at low energies and is large when the electron velocity is low enough for the  $\text{Br}^-$  to respond to with its full static polarizability. Thus, at the present, we must be prepared for the likelihood that (1), (2), or (3) or some combination of them is responsible for freeing electrons from the bromide ions.

The observation of the population inversion or overpopulation of the ionic limit, and more specifically, of the time required for relaxation from this condition, has two direct implications with respect to the spectroscopic measurement of photodetachment cross sections. First, in the previous work on halide absorption in dissociated salt vapors,<sup>5</sup> the assumption was made that the salt had reached equilibrium by the time observations were made of halide absorption spectra. The rates of equilibrium determined from the present measurements justify that assumption and lend support to the estimates of photodetachment cross sections of the halides previously made from spectroscopic data. Second, and presumably of more ultimate quantitative use, the present type of measurement, involving direct comparison of the intensity of the negative ion continuum and an atomic line, can eventually be expected to give very accurate photodetachment cross sections. One simply measures the ratio of absorption,  $I(\text{Br}^-)/I(\text{Cs}^0)$  when equilibrium is reached, and calculates concentrations from the partition functions. With our present results, we obtain a value for the absolute photodetachment cross section  $\sigma(\text{Br}^-, \lambda)$ , but this cross section is by no means as sure or precise a quantity as one can ultimately expect from this method. Unfortunately the Cs  $6s\text{-}8p$  doublet has an oscillator strength which is not well known; reported values from Ref. 16 are 0.342 and  $2.74 \times 10^{-3}$  for the two components (3889 and 3875  $\text{ \AA}$ ), while the semiempirical values of Stone are 0.317 and  $3.49 \times 10^{-3}$ . Our experiments give a value of

$$\sigma(\text{Br}^-, 3637 \text{ \AA})/f(\text{Cs}, 3875 \text{ \AA}) = 7.92 \pm 0.42 \times 10^{-15} \text{ cm}^2,$$

so that the uncertainty in the cesium  $8p$  oscillator strength  $f(\text{Cs}, 3875 \text{ \AA})$  contributes very significantly to the total uncertainty in a determination of  $\sigma(\text{Br}^-)$  in this work. Nevertheless, it does give us an experimental fix on the absolute magnitude of  $\sigma(\text{Br}^-)$ . Note that the wavelength 3637  $\text{ \AA}$ , 358  $\text{ cm}^{-1}$  above threshold, corre-

<sup>14</sup> M. R. C. McDowell (private communication).

<sup>15</sup> Based on estimates of  $\alpha(\text{Br}^-)$  for various alkali halides, as made by S. A. Rice and W. Klemperer, *J. Chem. Phys.* **27**, 573 (1957).

<sup>16</sup> G. Kvater and T. Meister, *Vestnik Leningrad. Univ.* **9**, 137 (1952) (exptl); P. M. Stone, *Phys. Rev.* **127**, 1151 (1962) (theoret); see also H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill Book Co., New York, 1964), Appendix 3.8.

sponds to a point on the photodetachment cross section curve of  $\text{Br}^-$  about two-thirds of the way up, between the threshold and the flat portion of the curve of  $\sigma(\nu)$ .<sup>17</sup> If we give equal weight to the experimental and semi-empirical values of the cesium oscillator strength, we obtain a new value of  $2.5 \pm 0.6 \times 10^{-17} \text{ cm}^2$  for the photodetachment cross section of  $\text{Br}^-$  at 3637 Å, corresponding to  $3.7 \times 10^{-17} \text{ cm}^2$  at 3600 Å, compared with

<sup>17</sup> R. S. Berry, C. W. David, and J. C. Mackie, *J. Chem. Phys.* **42**, 1541 (1965).

the previous value<sup>5b</sup> of  $1.2 (+1.2, -0.5) \times 10^{-17}$ . The discrepancy may be due primarily to an underestimate of the error in the previous experiments, to an error in the cesium oscillator strengths, perhaps to underestimated uncertainties in the present experiments or to any combination of these.

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## Atomic Arrangement of Au(100) and Related Metal Overlayer Surface Structures.\* I

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It has been shown, through analysis of simple overlayer structures consisting of a monolayer of Au or Ag on Cu(100) and Pd(100) surfaces, that Au atoms have an abnormal tendency to contract when positioned in a surface environment. This strong tendency for reduced interatomic spacing of Au surface layers is related to the atomically rearranged Au(100) surface, which consists of a hexagonal layer of Au atoms superimposed on a square array of substrate atoms. The driving force for rearrangement is interpreted in terms of the extreme sensitivity of the effective valency of Au to its atomistic environment. It is concluded that this interpretation of surface rearrangement is consistent with other unique properties of gold reported for binding energies of molecules in the vapor, and features of the band structure. In addition to providing information regarding the Au(100) surface structure, examination of metal overlayer structures has shown that pseudomorphism occurs during early growth stages of Ag and Au on the Pd(100) surface. Surface alloying of Au and Cu on the Cu(100) and on the Au(100) surfaces are also discussed.

### I. INTRODUCTION

Traditionally, it has been convenient to visualize metal crystal surfaces in terms of hard spheres which are attached to one another by nondirectional metallic bonds of equal strength. On the basis of this model, the stable atomic arrangement for a particular surface, defined by Miller indices (*hkl*), is one for which the number of missing interneighbor links is a minimum. Application of this pairwise interaction model to the (100) surface of fcc metal crystals predicts<sup>1</sup> that the most stable configuration is a nonreconstructed, atomically flat surface.

Experimental evidence now indicates that pairwise interaction models for metal surfaces are seriously oversimplified. For example, studies on the mobility<sup>2</sup> and binding<sup>3</sup> of metal adatoms on various single-crystalline tungsten surfaces demonstrate that the atomic configuration is a considerably more important factor than the number of nearest neighbors in determining,

respectively, the barrier to surface diffusion and the binding energy of adsorbed metal atoms. These highly significant results show that more careful consideration of the surface electronic structure of metals is needed to adequately explain many of their surface properties. In particular, it does not seem unreasonable that deviations in the surface electronic configuration from that of the bulk could also have considerable influence on surface atomic arrangement.

Low-energy electron diffraction<sup>4</sup> (LEED) as well as Auger electron spectroscopy<sup>5</sup> studies suggest strongly that the (100) surface of Au is reconstructed in the absence of stabilizing impurities. Since LEED patterns similar to those reported for the Au(100) surface have also been observed from Pt(100)<sup>6,7</sup> surface, it is probable that surfaces of these two metals are rearranged into a similar atomic arrangement. In view of the reproducibility with which the (1×5) superstructure

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<sup>3</sup> E. W. Plummer and T. N. Rhodin, *J. Chem. Phys.* (to be published).

<sup>4</sup> P. W. Palmberg and T. N. Rhodin, *Phys. Rev.* **161**, 586 (1967).

<sup>5</sup> P. W. Palmberg and T. N. Rhodin, *J. Appl. Phys.* **39**, 2425 (1968).

<sup>6</sup> S. Hagstrom, H. B. Lyon, and G. A. Somorjai, *Phys. Rev. Letters* **15**, 491 (1965).

<sup>7</sup> L. B. Lyon and F. A. Somorjai, *J. Chem. Phys.* **46**, 2539 (1967). See also P. W. Palmberg, *Structure and Chemistry of Solid Surfaces*, G. A. Somorjai *et al.*, Eds. (John Wiley & Sons, Inc., New York, 1969).