

## Chemical Overshoot: Thermal Dissociation of Alkali Halide Molecules

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The dissociation of CsBr molecules in shock-heated argon has been studied with time-resolved absorption spectroscopy. The time dependencies of the intensities of principal series lines of Cs<sup>0</sup> and of the photodetachment continuum of Br<sup>-</sup> show that the primary dissociation products are principally the ions Cs<sup>+</sup> and Br<sup>-</sup>. Attainment of chemical equilibrium concentrations of ions, electrons and neutrals occurs much more slowly.

According to the adiabatic noncrossing rule, the ground-state potential curves of diatomic alkali halide molecules extend to the dissociation limits corresponding to two neutral atoms in their ground states, despite the strongly ionic nature of the ground states near the equilibrium internuclear distances. However, most of the alkali halides afford classic demonstrations of the limitation of the adiabatic noncrossing rule; the continuous ultraviolet absorption spectra of these molecules indicate that the low-lying excited states, which should be bound if the noncrossing rule were obeyed, generally are in fact dissociating, corresponding to a violation of the rule.<sup>1,2</sup> In essence the reason for the violation is well-understood; it arises from the breakdown of the Born-Oppenheimer approximation for pseudocrossings occurring at large internuclear separations.

Here we report the initial results from investigation of a complementary problem, the mechanism of thermal dissociation of a diatomic alkali halide molecule in its ground electronic state. The results of our first study, of cesium bromide, show unequivocally that rapid thermal dissociation of alkali halides proceeds initially to the *ionic* dissociation limit. Achievement of the thermal equilibrium ratio of ions to atoms follows slowly after. In other words, the thermal dissociation process is shown to violate the noncrossing rule and to produce a large transient excess of ions.

The method is based on time-resolved absorption spectroscopy of shock-heated salts. The experimental procedure is as follows: (1) Five to ten milligrams of salt is introduced as a smoke into an argon-filled (30–100 Torr) shock tube by heating a salt-covered filament. (2) The incident, helium-driven shock heats the smoke particles sufficiently to vaporize them and produce diatomics, but not enough to dissociate the molecules to atoms. Typi-

cally, incident shock temperatures were ~1500°K. (3) The reflected shock initiates the process of interest by reheating the gas to temperatures sufficient to dissociate the diatomics. Typically, the equilibrium temperatures in the reflected shock were ~2800°K. Shortly before the incident shock passes the observation windows, a long-duration (~200 μsec) background flash is set off. The intensity of the lamp is constant after about the first 20 μsec. One can easily observe, in sequence, the unshocked gas for 50 μsec or more, the gas behind the incident shock (for about 30 μsec), and the gas behind the reflected shock, for 100 μsec or more. The absorption spectrum is recorded on a rotating drum camera spectrograph. The time resolution of the system is about 4 μsec based on the drum speed, the slit height, and the width of the light beam. The light beam traverses the 3.5-in. i.d. shock tube four times in a plane perpendicular to the tube axis. The beam width is 1 mm. Figure 1 shows the optical system. The apparatus is a modified form of one described previously.<sup>3,4</sup> The test section of the shock tube and the end wall are stainless steel. In salt-free shocks there is no indication from the spectra that impurities are being introduced from the end wall; with mild steel this was not the case. The windows are 1/8-in. sapphire.

The key data are the relative intensities of the 6s-*np* absorption lines ( $\lambda = 3888, 3876, 3617, 3611, 3480, 3477 \text{ \AA}$ ) of neutral cesium and of the photodetachment absorption continuum ( $\lambda \leq 3685 \text{ \AA}$ )<sup>4</sup> of negative bromide. Neither Cs<sup>0</sup> or Br<sup>-</sup> is detectable before the passage of the reflected shock; both are extremely clear afterward. Figure 2 shows a typical time resolved spectrogram.

The bromide continuum, readily identified by its sharp threshold, becomes exceedingly intense im-

<sup>3</sup> R. S. Berry, J. C. Mackie, R. L. Taylor, and R. Lynch, *J. Chem. Phys.* **43**, 3067 (1965) and earlier references therein.

<sup>4</sup> R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.* **37**, 2273 (1962).

<sup>1</sup> F. London, *Z. Physik* **74**, 143 (1932).

<sup>2</sup> R. S. Berry, *J. Chem. Phys.* **27**, 1228 (1957).

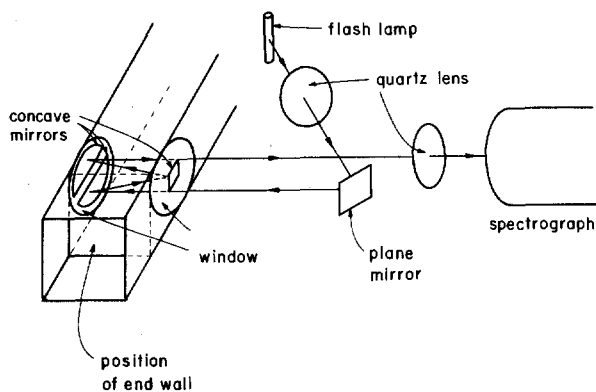


FIG. 1. Optical system.

mediately behind the reflected shock front. Typically, the maximum intensity, corresponding to nearly complete absorption, is reached within about  $4 \mu\text{sec}$ , the time resolution of the apparatus. This intensity then drops slowly, coming to within 10% of its long-time limiting value in roughly  $15 \mu\text{sec}$ . By contrast, the neutral atom absorption, e.g., the cesium lines at 3876 and 3888 Å, increase slowly and monotonically, and generally cannot be seen during the first 5–7  $\mu\text{sec}$  behind the reflected shock. The line and continuum intensities are essentially constant during the last 70–100  $\mu\text{sec}$  of observation time.

The concentration of cesium bromide molecules behind the incident shock front is of the order of  $10^{17}$  molecules/cm<sup>3</sup>; at 2800°K the equilibrium concentration of bromide ions is of the order of  $10^{15}$  ions/cm<sup>3</sup>. The intense bromide continuum immediately behind the reflected shock front corresponds to at least a threefold increase in bromide ion concentration over the equilibrium value.

The ion-atom relaxation time of 15  $\mu\text{sec}$  corresponds to about  $6 \times 10^5$  collisions. The time resolution of the apparatus is about  $2 \times 10^5$  collisions, which at present is our upper limit for the dissociation relaxation time. About 99.7% of the two-body collisions of any particle involve an argon atom; therefore, the relaxations are essentially argon induced.

In addition to time-resolved spectra taken near the end wall in the shock tube, we have also taken space-time ( $x-t$ ) photographs of the total light emission and of the light emitted by the most intense alkali resonance line, e.g., NaD with shocks into NaBr. The total light and alkali emission

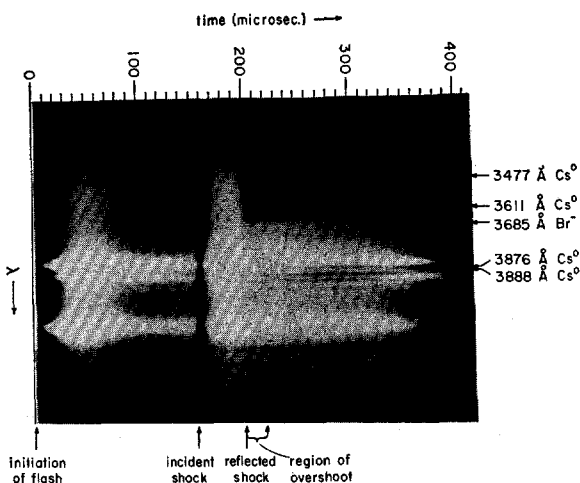


FIG. 2. Time-resolved spectrogram of the dissociation of cesium bromide.

photographs in the reflected shock are essentially indistinguishable. From these photographs it is clear that the space-time region in which the population anomaly occurs is limited to a zone of about 1 cm from the end wall of the shock, and decreases in duration with distance from the end wall. During the time of the anomaly, as defined by the absorption spectra, the emission photographs show the gas to be dark. Therefore, we know that the apparent lack of alkali absorption is not an artifact due to line reversal, but is a true indication of low concentration of neutral alkali atoms. The limited extent of the region of anomaly indicates that a slow-starting process, such as electron production, eventually leads to a mechanism for ion-atom equilibration considerably faster than any available when dissociation starts.

In conclusion, we should point out that the population ratio for alkali halides  $(M^+)(X^-)/(M^0)(X^0)$  at equilibrium and at *infinite* temperature varies between  $\frac{1}{2}$  for fluorides and  $\frac{1}{8}$  for iodides (because of spin-orbit splitting), so that the transient thermally induced inversion indicated here represents an extremely large deviation from equilibrium.<sup>5</sup>

#### ACKNOWLEDGMENT

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<sup>5</sup> For an account of an extended (later) study of this problem, see R. S. Berry, T. Cernoch, M. Coplan, and J. J. Ewing, *J. Chem. Phys.* 49, 127 (1968).