

the electron diffraction apparatus for this investigation. We wish also to thank Mr. G. Ferguson and Miss E. Bortle for assistance with the calculations.

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<sup>1</sup> See S. Mizushima and T. Shimanouchi, *Ann. Revs. Phys. Chem.* **7**, 447 (1956).

<sup>2</sup> W. S. Gallaway and E. F. Barker, *J. Chem. Phys.* **10**, 88 (1942).

<sup>3</sup> L. O. Brockway and L. S. Bartell, *Rev. Sci. Instr.* **25**, 569 (1954).

<sup>4</sup> Bartell, Brockway, and Schwendeman, *J. Chem. Phys.* **23**, 1854 (1955).

<sup>5</sup> Nomenclature follows that of L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955). Note, however, an error in this reference in two signs of Eq. (9). All four coefficients of sum in brackets should be positive.

## C<sub>2</sub> and CN Emission in the Shock Tube\*

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STRONG shock waves in the rare gases are often luminous,<sup>1</sup> though the flow behind them may not be. The experiments reported here were performed to discover the mechanisms responsible for this luminosity, which was first identified as C<sub>2</sub> and CN band emission by Turner<sup>2,3</sup> and by Rosa.<sup>4</sup> Turner ascribed the C<sub>2</sub> emission to collisional excitation of organic impurity fragments. Rosa found that, when organic impurities and air were present with argon in the expansion chamber gas of a shock tube, C<sub>2</sub> emission maxima occurred nearer the shock front than CN maxima. Previously, Green<sup>5</sup> had found that strong shocks in pure BrCN gave peak emission of the CN bands earlier (by about 6 μsec) than the intensity maximum for C<sub>2</sub> bands. The implication of these results is that peak emission near the shock by a configuration of atoms already present in the cold gas will generally precede (by a time of the order of μsec) emission from molecular species which are created behind the shock by recombination.

For shocks in the rare gases, we have found that, within our time resolution of 1 μsec, emission arising solely from recombination-formation of C<sub>2</sub> and CN can have peak intensity at the front, and that there is no qualitative difference between C<sub>2</sub> emission-*versus*-time profiles of this type and those occurring when C—C bonds are originally present in the gas. This has been done by including small amounts ( $p_1 \sim 10^{-2}$  to  $10^{-1}$  mm Hg) of CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and mixtures of CH<sub>4</sub> and NH<sub>3</sub> in the expansion chamber gas (neon at  $\sim 10$  mm Hg) prior to the shock arrival. This technique results

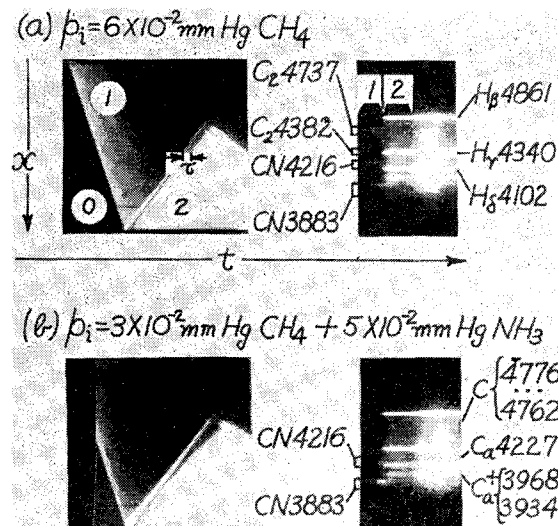


Fig. 1.

in two types of flow luminosity: (I) *transient* C<sub>2</sub> and CN emission at and immediately behind primary and reflected shocks, and (II) atomic and molecular emission behind reflected shocks which is *steady* after the ionization relaxation time  $\tau$  has elapsed; the temperatures are high enough that hydrogen and carbon lines, and C<sub>2</sub> and CN bands are easily visible (see Fig. 1). The remainder of this letter is devoted to the transient primary luminosity as it occurs in certain recombination experiments with CH<sub>4</sub> and CH<sub>4</sub>—NH<sub>3</sub>.

In Fig. 1, the left-hand pictures are distance-time photographs of the flow, taken through a narrow slit-window parallel to the flow; the slit is imaged on a moving film. The right-hand pictures are time-resolved spectra taken perpendicular to the flow direction, 4 cm from the end of the tube, so that both the primary (1) and reflection (2) luminosities are seen. The spectrograph speed is about  $f/5$ . In (a) and (b), respectively, primary shock velocities are  $3.318$  and  $3.373 \times 10^5$  cm/sec, initial pressures  $p_0$  are 7.827 and 7.788 mm Hg of neon with impurity (including  $\sim 10^{-2}$  mm Hg air leak), and temperatures  $T_0$  are 300.8 and 299.2°K. Approximate conditions behind the primary waves are  $p_1 \sim 530$  mm Hg,  $T_1 \sim 5000^\circ\text{K}$ , and behind the reflected waves  $p_2 \sim 2900$  mm Hg,  $T_2 \sim 11\,000^\circ\text{K}$ . The primary flow velocities  $u_1$  are about  $2.5 \times 10^5$  cm/sec;  $u_0 = u_2 = 0$ .

Microphotometer tracings of both  $x-t$  pictures show that the transient molecular emission has a high-intensity peak at the primary shock and decreases in intensity behind the shock. The spectra shown are not sufficient for demonstrating the true emission-*versus*-time profile because the length of the spectrograph slit image causes a time smearing. These spectra serve only to identify the radiating species. The existence of band emission by recombination at the primary shock implies dissociation of CH<sub>4</sub> and NH<sub>3</sub> immediately upon entry into the shock front. The ordered motion of the

primary flow makes the average energy available in collisions between rest gas molecules and primary flow atoms about twice that available *within* the primary flow at the temperature  $T_1$ ; therefore, immediate dissociation of molecules at the shock is reasonable. Molecular emission near the front and its later extinction cannot result simply from an overshooting and subsequent re-establishing of the dissociation equilibrium appropriate to the temperature  $T_1$ , since the degrees of dissociation for  $C_2$  and  $CN$  are roughly 0.9 in the primary flow.

We believe that the sequence of events following the entry of molecules into the shock front is as follows: (1)  $CH_4$  and  $NH_3$  are broken apart, leaving large numbers of C and N atoms in those states  $E'$  appropriate to combination into excited states of  $C_2$  and  $CN$ ; (2) this combination takes place and is followed (in  $\sim 10^{-8}$  sec) by radiation of the molecules into their ground states; (3) these ground-state molecules are dissociated into atoms whose states  $E$  do not allow recombination into excited molecular states; (4) the total emission gradually fades because there is no re-excitation mechanism for electronic transitions  $E \rightarrow E'$ .

Flow variations arising principally from viscosity may be responsible for some details of the primary luminosity; however, in experiments with weaker (nonluminous) primary shocks, the associated *reflected* shocks possess the same type of luminosity profile we have discussed.

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## Fluorescence Spectra of Uranium, Neptunium, and Curium

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**F**LUORESCENCE of  $AmCl_3$  and  $PuCl_3$  in dilute solid solution in a matrix of crystalline anhydrous  $LaCl_3$  has been reported previously.<sup>1,2</sup> We have since observed the fluorescence of  $U^{+3}$ ,  $Np^{+3}$ , and  $Cm^{+3}$  in a similar crystalline environment. Observed fluorescence lines and, for  $Cm^{+3}$ , absorption lines in the region 3000 to 8000 Å are listed in Table I. The fluorescence spectra were obtained by ultraviolet irradiation, as described previously,<sup>1,2</sup> although for curium ( $\sim 185 \mu g$   $Cm^{244}$  in 183 mg  $LaCl_3$ ) the radioluminescence is suffi-

TABLE I. Spectra of U, Cm, and Np in  $LaCl_3$   
(wavelength in angstroms).

|                             |   |              |  |                   |      |
|-----------------------------|---|--------------|--|-------------------|------|
|                             | CmCl <sub>3</sub> in LaCl <sub>3</sub> : fluorescence |              |  |                   |      |
| 4606<br>3984                | 4603  | 4588         | 4001                                   | 3995              | 3990 |
|                             | CmCl <sub>3</sub> in LaCl <sub>3</sub> : absorption   |              |  |                   |      |
| 3835                        | 3830  | 3787         | 3776                                   |                   |      |
|                             | NpCl <sub>3</sub> in LaCl <sub>3</sub> : fluorescence |              |  |                   |      |
| 6261<br>5118                | 6252<br>5060  | 6243<br>5046 | 6232<br>5030                           | 6219<br>4998      | 6208 |
|                             | UCl <sub>3</sub> in LaCl <sub>3</sub> : fluorescence  |              |  |                   |      |
| 6928<br>6482 <sup>a,b</sup> | 6915<br>5513  | 6898<br>5506 | 6812 <sup>b</sup><br>5452 <sup>b</sup> | 6800 <sup>b</sup> |      |

<sup>a</sup> Fluorescence line appears only at room temperature.

<sup>b</sup> Also appears in absorption.

ciently intense to be photographed on our 21-ft Wadsworth spectrograph.<sup>3</sup> The radioluminescence spectrum, aside from its lower intensity, is identical with that obtained by ultraviolet irradiation. The strong fluorescence group at 4000 Å continued to fluoresce in absorption experiments, and therefore has not been observed as an absorption line by us. It is now known, however, that this appears as a peak in the absorption spectrum of aqueous  $Cm^{+3}$ .<sup>4</sup>

The fluorescence of  $NpCl_3$  in  $LaCl_3$  was observed at a concentration of  $\sim 0.1$  atom percent  $Np^{237}$  similar to the  $CmCl_3$  preparation.

Because of the ready availability of natural uranium, solutions of  $UCl_3$  in  $LaCl_3$  up to 20 weight percent were prepared.

Attempts were made to incorporate  $UCl_3$  in  $NaCl$ ,  $SrCl_2$ ,  $BiCl_3$ , and  $MgCl_2$ . Although some uranium appeared to dissolve in some of the crystals, none of the products was fluorescent.

Some interpretation of the observed spectra is possible. The ground state of  $Cm^{+3}$  is  $^8S_{7/2}$ , with insignificant splitting by the hexagonal crystalline field of  $LaCl_3$ , so far as optical spectra are concerned. Multiplet structure therefore arises from crystal-field splittings of excited states. The three-component group of lines at 4600 Å therefore arises from a  $J=5/2$  level, the four-component group at 4000 Å from a  $J=7/2$  level, and the two doublets at 3830 Å and 3780 Å from  $J=3/2$  levels. The group at 4600 Å probably arises from the  $^6P_{5/2}$  level, that at 4000 Å from the  $^6P_{7/2}$  level (although it may be the  $^6I_{7/2}$ ), and the two groups with  $J=3/2$  from  $^6P$ ,  $^6D$ ,  $^6F$ , or  $^6G$ , or possibly from quartet  $S$ ,  $P$ ,  $D$ ,  $F$ , or doublet  $P$  or  $D$ , are entering.

The ground state of  $Np^{+3}$  is  $^5I_4$ . A preliminary analysis suggests levels at 60 and 110  $cm^{-1}$  above the ground state. The level of 19 870  $cm^{-1}$  is not split and therefore has  $J=0$ . The most reasonable assignment for this level is  $^5D_0$ , although  $^3P_0$  and  $^1S_0$  are possible.

The doublet at 16 070  $cm^{-1}$  is split by 25  $cm^{-1}$ . For this  $J=1$  level the possibilities are  $^5F$ ,  $^5D$ ,  $^5P$ ,  $^3D$ ,  $^3P$ ,  $^3S$ ,  $^1P$ .