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Department of Chemistry

Final Report

MOLECULAR FRAGMENTS IN SHOCK WAVES

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UMRI Project 02878

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ABSTRACT

The following are described within the report: (1) the design of an apparatus used for absorption spectroscopy of materials behind shock fronts, with provision for multiple-pass optics; (2) preliminary results based on shocks through alkali halides, giving evidence of dissociation and formation of diatomic alkali metal van der Waals molecules; (3) results on the fragmentation of diborane behind shock fronts, showing the formation, possibly, of an unstable polyatomic intermediate, then BH and finally polymeric species; and (4) preliminary results of flash photolysis of benzene, 2-diazonium carboxylate, directed toward the identification of benzyne, C_6H_4.

I. INTRODUCTION

Although this report is entitled final, it can be no more than a progress report. The work itself has been carried out at The University of Michigan up to this time. Now, after only half of the contract term has elapsed, the Chief. Investigator is assuming a position at Yale University, where, it is hoped, the work may continue under a new contract.

Much of the work carried out up to this time is in a tantalizingly in-complete stage. This will be particularly apparent in the descriptions which follow. Yet when the initial proposal was submitted, this incomplete stage was roughly where the Chief Investigator had optimistically hoped the work would be at this time. Consequently this report is submitted with a small de-gree of satisfaction, and with considerable eagerness about continuation of the work.

The work itself is described in the following sections in a qualitative and summarizing way. A Technical Operating Report now in preparation will describe the experimental work. It will contain detailed and quantitative ma-terial, including circuit diagrams, drawings of the apparatus, and many more spectrograms than the few included here.

The project, "Molecular Fragments in Shock Waves," was undertaken to in-vestigate, with spectroscopic techniques, the small molecules, atoms, ions, and radicals present behind shock waves, and to investigate related theoretical problems. The shock tube is a simple and convenient device for producing rather high temperatures for times sufficiently long for gases to reach thermal equi-librium and to be photographed, yet sufficiently short that the apparatus con-taining the gas remains stable and therefore simple to construct. Also, it was hoped that one might be able to observe transient species behind shocks. These would be species existing only during the interval between the arrival of a shock and the attainment of equilibrium. The first species of interest were gaseous negative ions such as Cl^- and OH^-, which are thermodynamically stable in reasonable concentration in the vapors of salts like Cesium chloride and hydroxide, at temperatures of $3000°K$ and above. Among the other species of interest have been boron hydride fragments such as BH_3 or BH_2. Not enough is known about these latter two to permit prediction of their stability. (In fact, spectroscopic studies might answer some of the open questions about the boron-hydrogen bonds.) The efforts of this project have been directed prin-cipally along these two lines. Ultraviolet flash absorption spectroscopy has been the principal technique: a shock wave passing down a steel tube triggers

an electrical pulse which, after a previously selected time delay, triggers flash lamp. The flash lamp is discharged while the shock-heated gases are passing between two quartz windows on opposite faces of the shock tube. The light of the lamp is led into a spectrograph to produce a photographic record. The apparatus is shown schematically in Fig. 1.

The next section describes the apparatus and the manner in which it functions. The third section deals with the work, both experimental and theoretical, on alkali halides and their dissociation products. The fourth section is a review of the work done on shocks in diborane. The fifth section describes recent results of an excursion into flash photolysis, carried out in collaboration with Professor R. M. Stiles of The University of Michigan. The last section is an outline of the future work which it is hoped may follow that described in Sections III, IV, and V.

II. APPARATUS

The shock tube itself is a very simple device: a tube of 1/4-in. steel, twenty feet long, with a square cross section, its inside diameter is 3-1/2 in. The tube is divided principally into two parts; the first five-foot length can be separated from the remainder by insertion of a plastic or metal diaphragm. Through standard filling connections, gas (usually hydrogen) is put into the five-foot section at high pressures of about 250 psi. The gas to be studied is put into the longer section, at a very low pressure (usually of the order of 1-5 mm Hg) in the presence of a relatively inert carrier such as argon or nitrogen, which itself exerts a pressure of about 2 cm Hg. The diaphragm is allowed to burst; "Mylar" plastic diaphragms are generally punctured with a magnetically driven needle, while scribed aluminum circles burst spontaneously under the pressure of the gas. The hydrogen, released at high pressure, rushes into the low-pressure section, acting as a piston and rapidly compressing the low-pressure gas. This compression propagates as a shock, travelling down the tube at a nearly constant velocity of the order of 2 mm/μsec, or of about five to six times the speed of sound in argon at room temperature. Knowledge of this velocity, of all the initial partial pressures and density of the unshocked gas, and of all the pertinent chemical equilibrium constants, permits evaluation of the temperature and partial pressures in the heated gas behind the shock, when it reaches equilibrium. This equilibrium occurs at temperatures of the order of 3000°K for most of the experiments described here.

Three gauges measure the velocity of the shock. Each gauge is a glass rod inserted in the shock tube so that its squared end fits flush with the inner wall of the tube. The glass rod has deposited on it a very thin layer of platinum, which acts as a temperature-dependent resistance. This resistance acts as one arm of a simple bridge, and when the resistance changes slightly as the shock passes, a small voltage signal is developed. This can be amplified and formed into a sharp pulse. The first gauge acts as a trigger for an oscilloscope which then displays all the pulses as a function of time. Since the sweep rate of the oscilloscope is calibrated and the distance between the gauges is known, the oscilloscope trace provides a measurement of the shock velocity and of the change of velocity, if any. This trace is conveniently photographed with a Polaroid Land Camera.

The signal from the first gauge can also be sent into a delay circuit which leads to the flash lamp trigger. Alternatively, photocells may be placed at windows near or at the point where the flash lamp is located, and these photocells may be used to trigger the flash. Customarily, the light output of one photocell is displayed on the oscilloscope with the gauge traces,

and the output from the other photocell, if it is used, is amplified and sent to the delay- and-trigger circuit. Circuit delays are variable from about 20 $\pm$ 2 μsec to about 1200 $\pm$ 20 μsec. By using the various trigger impulses, the flash lamp may be fired at any time during the passage of the hot gases in front of the observation windows The electronics are indicated schematically in Fig. 2.

The flash lamp itself is a quartz capillary containing air at a pressure of about 5 mm Hg. Approximately 75 joules are dissipated in about 20 μsec, with most of the light intensity appearing in about the first 10 μsec. The lamp provides a smooth continuum, except for a few silicon lines, SiO bands, and aluminum lines.

Light from the flash can be passed directly through the shock tube into the spectrograph, or, as happened more often in the experiments described here, can be passed through the hot gas three times before it enters the spectrograph. For absorption spectroscopy, the latter method has proved of very considerable aid. The spectrograph used until now has been a Hilger medium quartz model. Spectrograms have been taken on Ilford Zenith, HPS, Rapid Process Pan and Ordinary plates, and on Eastman 103F plates.

III. DISCUSSION

A. ALKALI HALIDES

1. Experimental

The first problem which was undertaken when this project began was an investigation of the absorption spectra of alkali halides, and particularly of the atoms and ions produced when these salts are dissociated by a shock wave. Simple statistical-thermodynamic calculations show that the equilibrium reactions

$$MX \rightleftharpoons M^0 + X^0 \tag{1}$$

and

$$MX \rightleftharpoons M^+ + X^- \tag{2}$$

(where M is an alkali metal and X is a halogen) lie far enough to the right, at temperatures of 3000-4000°K, that the atomic and ionic species should be readily detectable. Table I contains equilibrium constants for ionic dissociation, as in (2), above, for the alkali halides at 3000° and 4000°K. These have been computed for all the alkali halides where sufficient data were available.

The ionic partial pressures can easily get to a significant fraction of the total pressure, as the above constants show. The atomic partial pressures are of the order of twelve times the atomic at such high temperatures; the twelve-fold degeneracy (neglecting spin-orbit coupling) of $M^0 + X^0$ is by far the predominant factor in the ratio of P_{M^0}/P_{M^+} and P_{X^0}/P_{X^-}. From these figures, one can suppose that sufficient X^- might be available to observe its continuous absorption spectrum.

Shocks of alkali halides were conducted as follows. A strip of cleansing tissue was impregnated with a concentrated solution of the salt being studied and then dried. This strip was placed across the shock tube, held between flanges of two sections of the shock tube. The shock wave disintegrated the paper and vaporized sufficient salt to show clear absorption spectra of alkali atomic lines. The time at which the spectral flash lamp was triggered did not seem to be critical; the absorbing atoms appeared to move at roughly the theoretical velocity of the argon carrier gas behind the shock front, and to persist for some time after, perhaps even to the cold interface. There seemed to be a little slowing of the shock after the tissue was picked up, as one

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would expect when dissociating species are present. Most of the work was done on CsCl, CsF, and RbCl, these being the most favorable species for ion production.

TABLE I

DISSOCIATION CONSTANTS K_p (atm) FOR

$$MX(^1\Sigma^+) \rightleftharpoons M^+(^1S_0) + X^-(^1S_0)$$
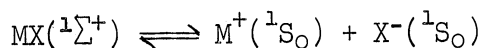
A. 3000°K

	F	Cl	Br	I
Li	1.608×10^{-10}		7.35×10^{-7}	4.062×10^{-6}
Na		4.451×10^{-6}	3.537×10^{-6}	1.498×10^{-5}
K		5.05×10^{-5}	9.85×10^{-5}	1.096×10^{-4}
Rb	8.25×10^{-7}	2.6×10^{-4}	1.019×10^{-4}	2.527×10^{-4}
Cs	1.263×10^{-6}	1.644×10^{-4}	2.99×10^{-4}	4.499×10^{-4}

B. 4000°K

	F	Cl	Br	I
Li	4.815×10^{-7}		1.471×10^{-4}	4.866×10^{-4}
Na		8.02×10^{-4}	4.220×10^{-4}	1.154×10^{-3}
K		2.932×10^{-4}	4.591×10^{-4}	4.596×10^{-3}
Rb	1.453×10^{-4}	9.61×10^{-4}	4.542×10^{-4}	8.454×10^{-3}
Cs	1.934×10^{-4}	6.62×10^{-4}	9.514×10^{-4}	1.218×10^{-3}

Typical spectra are shown in Figs. 3, 4, and 5. These were all taken with a three-pass arrangement for the light, so that the actual light path length was approximately 10-1/2 in. There are several features of interest in these spectra; before discussing them, however, it would be well to point out that no verifiable negative ion continua, alkali atom series limit continua or alkali halide fluctuation bands have been recorded up to the time of writing. The Principal In-

vestigator and Dr. G. N. Spokes still intend to look for and hope to find these continua; the means for doing this is discussed in the final section of this report.

Returning to the spectra, we find well-marked doublets of the principal series of the alkali atoms. Both rubidium and cesium appear in those spectra which were taken when one salt had been used after the other without the tube being cleaned in the interim. This caused no difficulty since the two series are so well separated. Up to about six principal series doublets have been detected. Certain of these appear not as doublets, but as triplets. These are the absorption spectra due to Rb_2 and Cs_2 "polarization molecules" described by Kuhn,[1] Rompe,[2] Loomis and Kusch,[2] more recently by Jefimenko and Gwinn,[4] and many others. Takeyama and Guttman[5] report emission spectra from shocked sodium salts, which they attribute to analogous Na_2 molecules. In the absorption spectra of Rb and Cs shown in Figs. 3-5, it is quite clear that the intensity of the "third lines" associated with the atomic doublets do drop off in intensity much faster than do the atomic lines themselves, indicating the consistency of the assignment to diatomics.

It is interesting that the C_2 Swan bands are detectable in several of the spectra. Presumably the C_2 is a decomposition product of the tissue used to support the alkali halide salt. The 0-0, 1-1, and 2-2 bands are all discernible the last being quite faint. The intensities are compatible with a temperature of the order of 2500-2800°K, which is in agreement with the temperatures determined from oscillographic traces monitoring the velocity of the shock waves.

When the work on alkali halides reached the point just described, the decision was made to modify the apparatus slightly. Two main changes were undertaken. First, the considerably improved absorption spectra obtained with three passes of the light through the tube prompted the investigators to construct a three-mirror system, like that described by White.[6] With this system, and a considerably stronger spectral flash, it was hoped that up to sixteen or perhaps even thirty-two passes could be obtained. The second modification was the construction of an inlet system which would permit the salts to be introduced as smokes or dusts, rather than as solid material impregnated into tissue. This was done in the hope that higher concentrations of salt would increase the absorption. In fact, to make this process effective for producing ions, higher temperatures (i.e., stronger shocks) would have to be used: in the range of operation until now, the partial pressures of dissociated species are high enough that any increase in total salt pressure would significantly decrease the amount of dissociation. The existing apparatus is nonetheless quite capable of sustaining the stronger shocks. The multipass system, stronger flash lamp, and salt-introduction system are all completed and ready for installation. They have not been put into use yet because the investigators decided to try to follow and complete the work described in the following section.

It is hoped that the alkali halide work can continue in the immediate future.

2. Theoretical

The Chief Investigator has been interested for some time in the electronic structure of alkali halide molecules, and in the relationship between various approximate representations of the wave-functions of molecules. In the case of the alkali halides, two representations have been used extensively. Townes and Dailey[7] represented alkali halide molecules with mixtures of spherical-ion functions and covalently-bound atomic functions to compute quadrupole coupling constants; Benson and van der Hoff[8] used a similar representation to construct a potential energy curve for HF. Sternheimer and Foley[9] and later Burns[10] have used polarized-ion functions to compute quadrupole coupling constants, while Das and Karplus[11] and others have used a variational method which is another form of the polarized-ion model to compute the same constants. Karo and Allen[12] have used a polarized-ion model similar to Sternheimer's to treat the potential energy curve of HF.

It has been pointed out many times that the two approaches, of polarized functions and ionic-plus-covalent functions, correspond to two different unperturbed basis sets, and that the only choice to make between them is one of convenience and of rapidity of convergence. To shed some light on this question, Mr. Hsien C. Hsiung has been computing the overlap integral, or alternatively, the degree of similarity of the two different types of functions. Mr. Hsiung, a graduate student in chemistry at The University of Michigan, was forced to drop this work for a time to complete course requirements. He has returned to the problem and currently expects to complete the work before the end of this summer, 1960.

Meanwhile, Miss Chi-hua Wu (now Mrs. Hsiung) has been working on a variant of the method of Das and Bersohn[11,13] to permit one to compute alkali halide potential curves with the accuracy attained by Karo and Allen[12] for the HF molecule. It is hoped that from this one may eventually understand in sophisticated quantum-mechanical terms why the simple classical Born-Mayer-Rittner ionic model[14] gives such remarkably good predictions of alkali halide properties, despite its apparent unreality. The work of Mrs. Hsiung is not completed, but is well along, ready now for numerical computation. The large amount of arithmetic associated with the final computation make it likely that high-speed machine computation will be very desirable.

B. FRAGMENTS FROM DIBORANE

When the spectroscopic work on the alkali halides was suspended while the mirror system was being constructed, Dr. Spokes and the author of this report began an investigation of the spectra behind shocks in diborane, B_2H_6. It had been suggested in the original proposal that the technique of absorption spectra behind shocks might be very useful for detection of species such as BH_3 or BH_2. Neither of these species has been reported at the time of this writing. The production of such species could be affected either by the thermodynamic properties of all the species involved, such as H_2, solid and gaseous boron and so forth, if the species were detected under equilibrium conditions, or by the explicit process in which they were formed, if they were detected as transients. (A brief mention of transient species was made previously.)

One can try to predict the structure and spectra of BH_2 and BH_3 with the aid of semiempirical molecular orbital theory. Following reasoning analogous to that of Mulliken[15] or Walsh[16] one predicts that

1. linear BH_2 would have the ground state

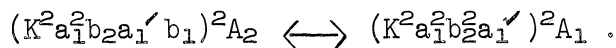$$K^2(a\sigma_g)^2(a\sigma_u)^2 \, \pi_u \, , \quad {}^2\Pi_u \; ;$$
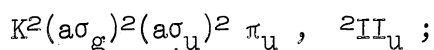
2. the π_u orbital would split when the molecule bent, and that the lower component would have symmetry a_1 and would have lower energy if the molecule is bent than if the molecule is linear. The ${}^2\Pi_u$ state would, moreover, be subject to a bending Renner effect like that of NH_2.[17] Therefore it is quite possible that BH_2 would be a bent molecule.

3. If BH_2 were bent, it would have a large number of low-lying allowed (parallel-type) transitions, of which the strongest would be

$$(K^2 a_1^2 b_2 a_1'^2), \; {}^2B_2 \longleftrightarrow (K^2 a_1^2 b_2^2 a_1'), \; {}^2A_1(\text{ground state}),$$
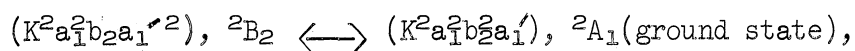
and the two doublet-doublet transitions of the type

$$(K^2 a_1^2 b_2 a_1' b_1)\,{}^2A_2 \longleftrightarrow (K^2 a_1^2 b_2^2 a_1')\,{}^2A_1 \; .$$

The former of these might lie at about $43000\,\text{Å}$, and the latter in the region of $4000\,\text{Å}$, if one uses the isoelectronic CH as a model. There should also be a low-lying weak (perpendicular) transition

$$(K^2a_1^2b_2^2b_1)^2B_1 \longleftrightarrow (K^2a_1^2b_2^2a_1)^2A_1 \, ,$$
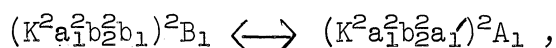
which could be in the infra-red region.

There are also many allowed transitions predicted further toward short wavelengths than those mentioned.

By contrast, the BH_3 molecule is very probably planar, rather than pyramidal. If this is the case, there would probably be only one low-lying transition,

$$(K^2a_1^2e^3a_2)^1A_1 \longleftrightarrow (K^2a_1^2e^4)^1A_1 \text{ (ground state)},$$
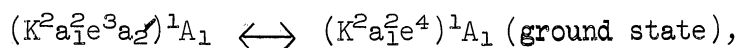
which would be like a $\pi \longleftrightarrow \sigma$ transition and therefore relatively weak. The stronger transitions would all probably lie in the vacuum ultraviolet region.

Also, the BH_2 species is probably quite unstable; BH_3 might, perhaps be expected to survive for a reasonably long time. Actually, many other species might be involved in shocks in B_2H_6, since it is well known that polymers are formed when B_2H_6 decomposes. It was hoped when this line of work was undertaken that the simpler species such as BH_2 and BH_3, if detectable at all, could be sorted out from more complicated systems by the use of deuterium substitution.

With the preceding discussion as a background, we may look at the results obtained when diborane was examined under shock conditions. Most of the experiments were run with total low pressures of approximately 2.2 cm Hg of argon mixed with diborane; the diborane comprised about one-thirtieth of this pressure. The driving gas was hydrogen, at pressures of the order of 200-250 psi.

The first spectra, to the surprise of the investigators, showed total absorption. Comparison spectra of the gases before and after the shock wave showed no absorption. Then, by varying the delay between the time of passage of the shock front past the observation window and the time at which the spectral flash lamp was triggered, it was possible to find a time at which the only absorptions detectable were lines of silicon. (SiH_4 was a known contaminant in the early samples of B_2H_6.) Eventually, careful variation of the delay time led to a self-consistent model for the behavior of B_2H_6 under shock conditions. This model is a result of the interpretation of the spectra of Figs. 6-10. The interpretation is as follows, in terms of a typical experiment.

1. A shock of Mach 6 (or 1.8 mm/microsecond) reaches the observation window. The pressure ratio across the shock is 46, the density ratio is 3.8, and, neglecting the dissociation of B_2H_6, the temperature is 3660°K behind the shock. For approximately 90 microseconds of laboratory time, corresponding 340 seconds of heating for the compressed diborane, nothing detectable happens to the diborane. Any SiH_4 present is decomposed sufficiently to show strong silicon lines by the time twenty microseconds of laboratory time have elapsed.

2. At approximately 93 microseconds after the arrival of the shock, weak continuous absorption appears in the ultraviolet, and many strong bands, diffuse and sharp, appear in the blue, violet and near-ultraviolet region. No BH bands are detectable at this stage.

3. After approximately 95 microseconds, the much strengthened continuous absorption has moved through the entire ultraviolet, almost obscuring the visible region. At this time BH bands are clearly visible at 4331, 4367, and 4433Å, corresponding to the heads of the 0-0, 1-1 and 2-2 bands of the $^1\Pi \leftarrow {}^1\Sigma$ system.[19]

4. Thereafter, the continuous absorption or scattering becomes increasingly stronger until the entire spectrum is wiped out.
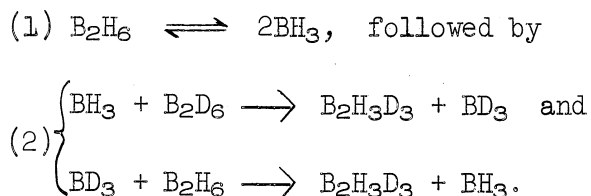
These four stages point very strongly to a mechanism in which Stage 1 represents a long induction period; Stage 2 is a period in which fragmentation of the B_2H_6 into polyatomic species occurs, together with a small amount of polymerization; Stage 3 corresponds to complete fragmentation of B_2H_6 all the way to diatomic BH species, together with considerable polymerization; and finally, the fourth stage corresponds to the last stages of growth of polymers.

The time resolution of approximately one microsecond is an interesting result of the very short time necessary to initiate the flash and of the rapidity with which total absorption sets in. In effect, the totally absorbing portion of the shocked gas acts as a shutter, so that the effective duration of the flash is the interval between the initiation of the flash and the time at which total absorption occurs. This mechanism was pointed out by Dr. Spokes.

The BH spectrum was first confirmed by comparing the absorption with emission bands produced in a hollow cathode lamp. This was the method first used to excite BH emission.[18] The hollow cathode spectrum, Fig. 11, is produced from a mixture of BCl_3 and H_2, with the latter being in excess, and the total pressure, approximately 1 mm.

The BH spectrum was further confirmed by producing the BD species in shocks through B_2D_6. The spectrum of the $^1II \longleftarrow {}^1\Sigma$ transition of BD lies in almost exactly the same place as that of BH. In this study, prominent absorptions have been found at 4425, 4387, 4349, 4334, 4327, 4309, and 4260Å. The BH Q-branch heads observed in this study are those at 4331.6, 4367.3, and 4433.7Å.[20] The 0-0 Q-branch head of BD seems to be at 4327. Careful measurements and identification of these absorptions is in progress now. Also, at the time of writing, experiments are in progress to try to find for B_2D_6 the "polyatomic" bands observed in the B_2H_6 work. It is hoped that experiments with B_2D_6, followed by others with equilibrated mixtures of B_2D_6 and B_2H_6 (see below regarding the exchange reaction) will permit the identification of the "polyatomic" bands. The BD bands are shown in Fig. 12.

Turning now to an interpretation of the remarkable behavior of the shocked diborane, one finds that the possibility of free radicals from B_2H_6 has been suggested many times. Perhaps one of the most conclusive studies was that of Maybury and Koski,[20] who showed that the exchange reaction of B_2H_6 and B_2D_6 could be explained entirely on the basis of a homogeneous free-radical mechanism

$$(1) \quad B_2H_6 \rightleftharpoons 2BH_3, \quad \text{followed by}$$

$$(2) \begin{cases} BH_3 + B_2D_6 \longrightarrow B_2H_3D_3 + BD_3 \quad \text{and} \\ BD_3 + B_2H_6 \longrightarrow B_2H_3D_3 + BH_3. \end{cases}$$

The possibilities of the formation of BH_2 and BH_4, or $2BH_2 + H_2$ have been discussed by Parry and Edwards.[21] The former is possible when B_2H_6 reacts with bases like NH_3. The latter is known to occur for B_4H_{10}, and B_2H_6, on standing at room temperature, slowly gives off hydrogen. Parry and Edwards[21] also review the evidence indicating that high-molecular-weight boron hydride polymers are actually $(BH)_n$, and that the end result of boron hydride pyrolysis is the combination of BH fragments into these polymers. The experimental work of this project is very much in support of this view, as the figures show.

Direct observations of the kinetics of pyrolysis of diborane at temperatures under 200°C were carried out by Clarke and Pease,[22] and by Bragg, McCarty, and Norton.[23] Both of these studies indicated free radical mechanisms, presumably involving BH_3. Bragg, McCarty, and Norton found evidence suggesting that there was no time-dependent intermediate species in their reaction. They, of course,

were not working at temperatures of 3000°C, nor could they observe events of ten-microsecond duration. Both of these studies indicated some loss of hydrogen which would be consistent with the hypothesis of BH_2 formation at high temperatures.

In any case, the present study has definitely established that BH is produced behind shocks through B_2H_6, and that the BH appears only after a very long induction period. The work indicates that the BH is formed very rapidly and reacts very rapidly to give a product which is perhaps polymeric $(BH)_n$. The work suggests that very transient polyatomic species may be present just before the BH radicals are formed. It is possible that these species may be BH_2, and lastly, it is a consistent hypothesis that BH_3 is present and could be detected via its vacuum ultraviolet spectrum. A paper describing this work is in preparation and will be completed when the B_2D_6 and mixed-species experiments are concluded.

C. FLASH PHOTOLYSIS

The interest of the investigators of this project in molecular fragments has led to work carried out in cooperation with Professor R. M. Stiles of The University of Michigan. Professor Stiles[24] has recently found evidence that the species

$$\begin{array}{c} \text{(benzene ring with } CO_2^- \text{ and } N_2^+ \text{ substituents)} \\ I \end{array}$$
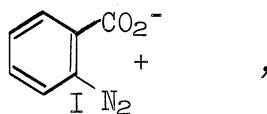
on gentle heating, loses CO_2 and N_2 to form C_6H_4, benzyne, usually drawn as

$$\begin{array}{c} \text{(benzyne ring structure)} \\ II \end{array}$$

With Stiles, we have undertaken a series of experiments to try to produce benzyne by flash photolysis and to obtain its absorption spectrum. The flash and delay units which form the heart of the shock spectroscopic work are exactly the kind of equipment necessary to carry out flash photolysis spectroscopy Mr. Wayne Warren, an undergraduate at The University of Michigan, has been working on this project to adapt the apparatus for flash photolysis.

At the time of this writing, the results of the flash photolysis work are as follows.

(1) A single flashing of a thin film of thinly deposited solid Compound I in an evacuated quartz tube produces a yellow dust which settles nearly uniformly throughout the tube. Two gases are produced, which appear to be N_2 and CO_2; their quantity indicates that at least 25% of the starting material is photolyzed in a flash.

(2) Diphenylene (III) and triphenylene (IV)

III   IV
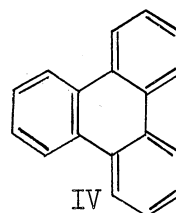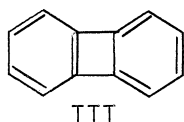
have been isolated and characterized as reaction products, in quantities consistent with the amounts of gas produced. The vapor spectrum of diphenylene is detected in the sample tube after photolysis. At the time of writing, no attempt has been made to find the diphenylene spectrum at times shorter than five seconds after the photolysis.

(3) At 100 and 140 microseconds after the initiation of the photolysis, no diphenylene spectrum is detectable.

(4) At approximately 30 microseconds after the initiation of photolysis, an absorption spectrum is produced which is not that of diphenylene. This spectrum has a broad absorption in the region 2400-2200Å with a possible maximum at about 2390Å, and a much stronger absorption beginning at about 2200Å.

It seems very possible that this absorption is due to the benzyne molecule itself. Experiments are in progress to try to get more conclusive identification of the species.

IV. MISCELLANY AND FUTURE PLANS

In connection with the diborane work, and particularly to produce known BH spectra, a graduate student, Mr. Paul Palmer, has constructed a hollow-cathode lamp. Mr. Palmer intends to work on shock-tube problems or on a theoretical problem unconnected with this project, as his doctoral research problem. The hollow-cathode work provides a chance for him to learn spectroscopic techniques and at the same time provide worthwhile and useful information. He will doubtless try to look for the "polyatomic" bands by examining B_2H_6 in his lamp. He holds a National Science Foundation fellowship and is therefore not supported directly by this project.

Future work contemplated by the Principal Investigator lies at this point, along the three lines followed until now. First, the alkali halide—negative ion work is ready for its next stage. The apparatus is ready; if the work is permitted to go on when the Chief Investigator completes his move to Yale University, it should be among the first problems studied.

The second problem which the Chief Investigator would like to study is pertinent to the diborane work. Specifically, it would perhaps be fruitful to search in the vacuum ultraviolet region for BH_3 radicals. Yale University has contemplated the purchase of a small vacuum grating spectrometer which would be ideal for this purpose. The necessary modifications to the shock tube would be extremely simple, and the knowledge gained from the B_2H_6 work so far would be of great assistance in any further investigation of this system.

Third, the flash photolysis has proven stimulating enough, yet closely enough related to the shock tube problems, that the Chief Investigator would like very much to try to study benzyne itself if the present experiments are successful, and to examine photolysis of other species suggested by the work of Dr. Stiles and of Dr. Michael Martin, also of The University of Michigan.

V. SUMMARY

The project "Molecular Fragments in Shock Waves," has been underway for approximately one and one-half years. A shock tube has been constructed and put into operation. Over 100 shocks have been run and photographed, mostly with absorption flash spectroscopy.

Work on alkali halides and negative ions showed absorption spectra of alkali metal atoms and diatomic alkali and carbon molecules. Optical equipment has been redesigned and rebuilt and this project is ready for further investigation.

Work on diborane has led to a suggested chain-reaction mechanism for the fragmentation and polymerization of B_2H_6. BH bands and "polyatomic" bands possibly due to BH_2 have been observed.

Other apparatus just completed and ready for use includes a hollow-cathode lamp and a high-energy flash photolysis apparatus. The former is to be used with boron studies and the latter, with R. M. Stiles, to search for the spectrum of C_6H_4, benzyne. Results of preliminary experiments indicate that benzyne is produced by flash photolysis.

The Chief Investigator would like to apologize for the very incomplete condition of the work described in this report. Due to the early termination of the contract under which this was carried out, it was not possible to do any more with the problems than has been described herein. It is hoped that further investigations may be carried out to complete at least some of the work.

VI. ACKNOWLEDGMENTS

VII. BIBLIOGRAPHY

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TANK

PISTON SECTION

LOW–PRESSURE SECTION

A

B

C

D

D

E

E

F

G

G

H

G

I

FILLING
SYSTEM

PUMP
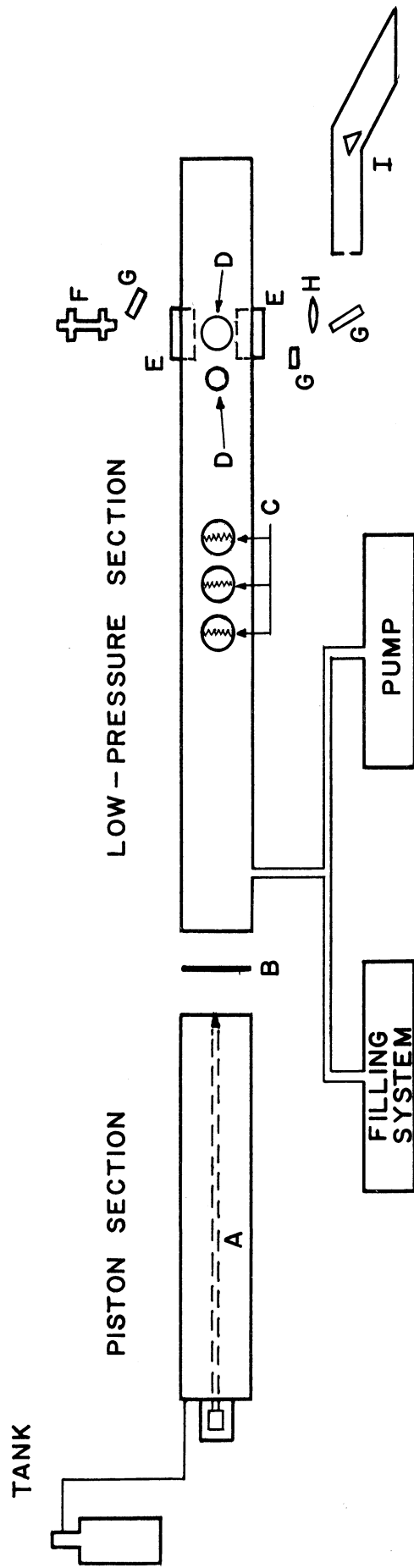
KEY:

A - MAGNETICALLY-DRIVEN PIN

B - DIAPHRAGM

C - RESISTANCE GAUGES

D - PHOTOCELL WINDOWS

E - QUARTZ WINDOWS

F - FLASH LAMP

G - MIRRORS

H - COLLIMATING LENS

I - MEDIUM QUARTZ SPECTROGRAPH

Fig. 1. Schematic Diagram of Shock-Tube Apparatus.

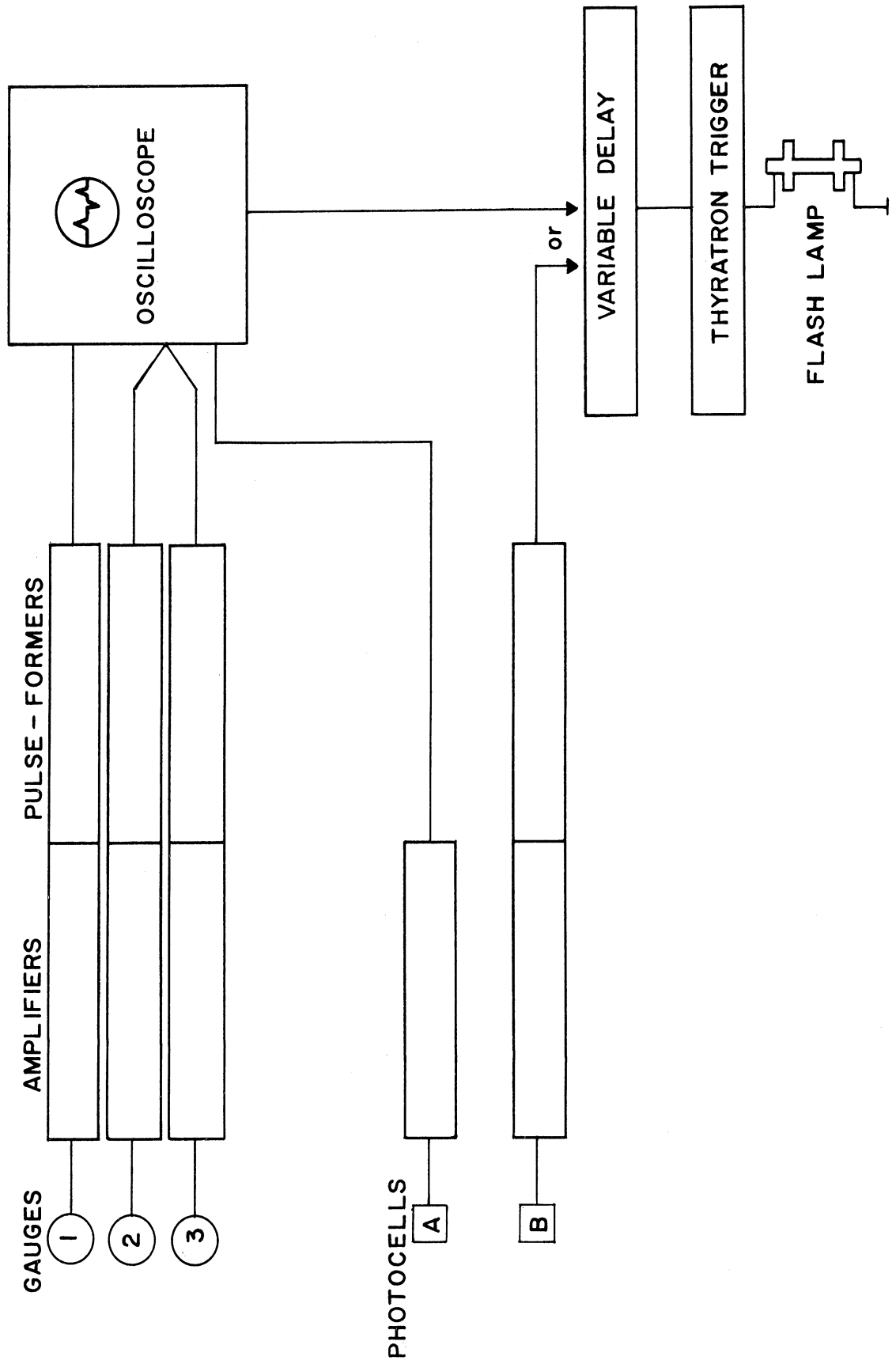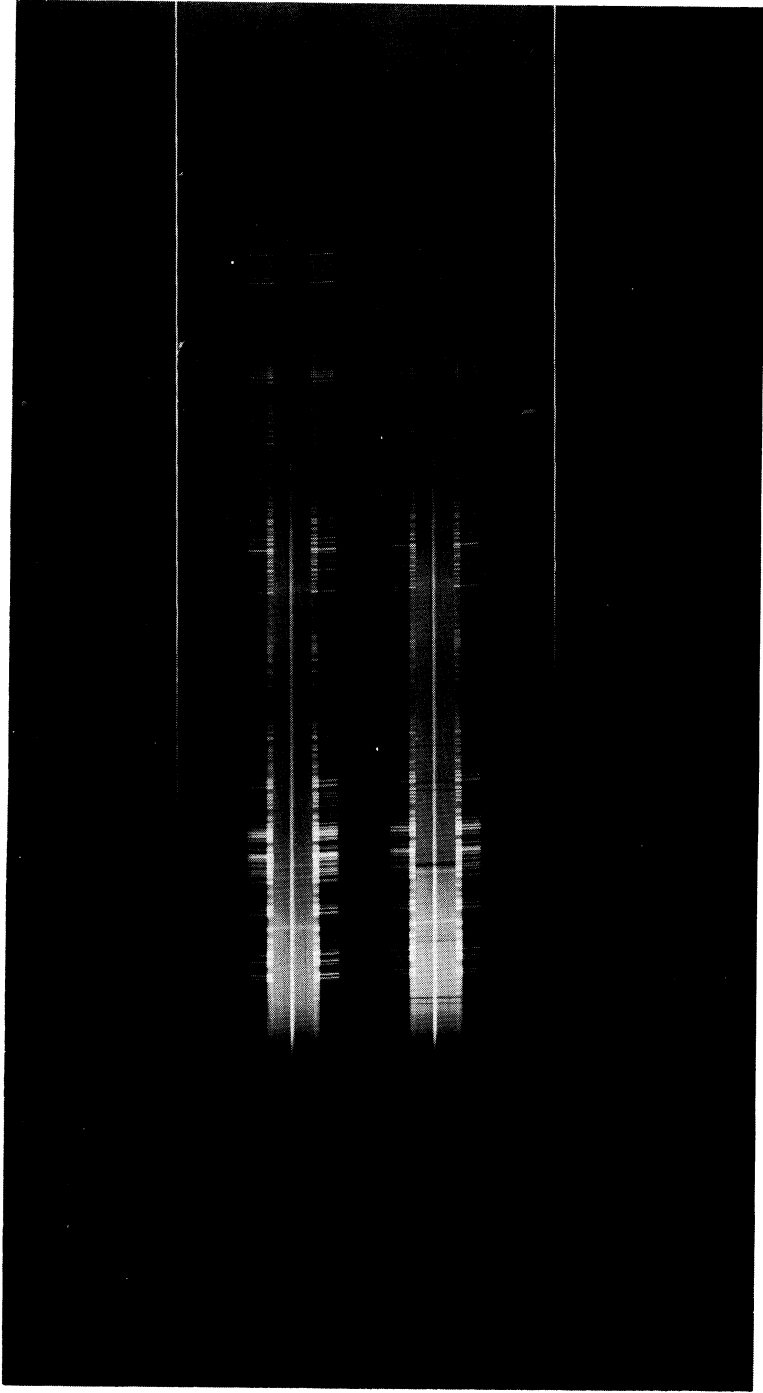Fig. 2. Schematic Diagram of Timing and Triggering Circuits.

Fig. 3. Absorption Spectrum of Shocked CsCl.
Top: flash lamp comparison
Bottom: absorption spectrum behind shock.
Dark lines are absorption due to cesium.
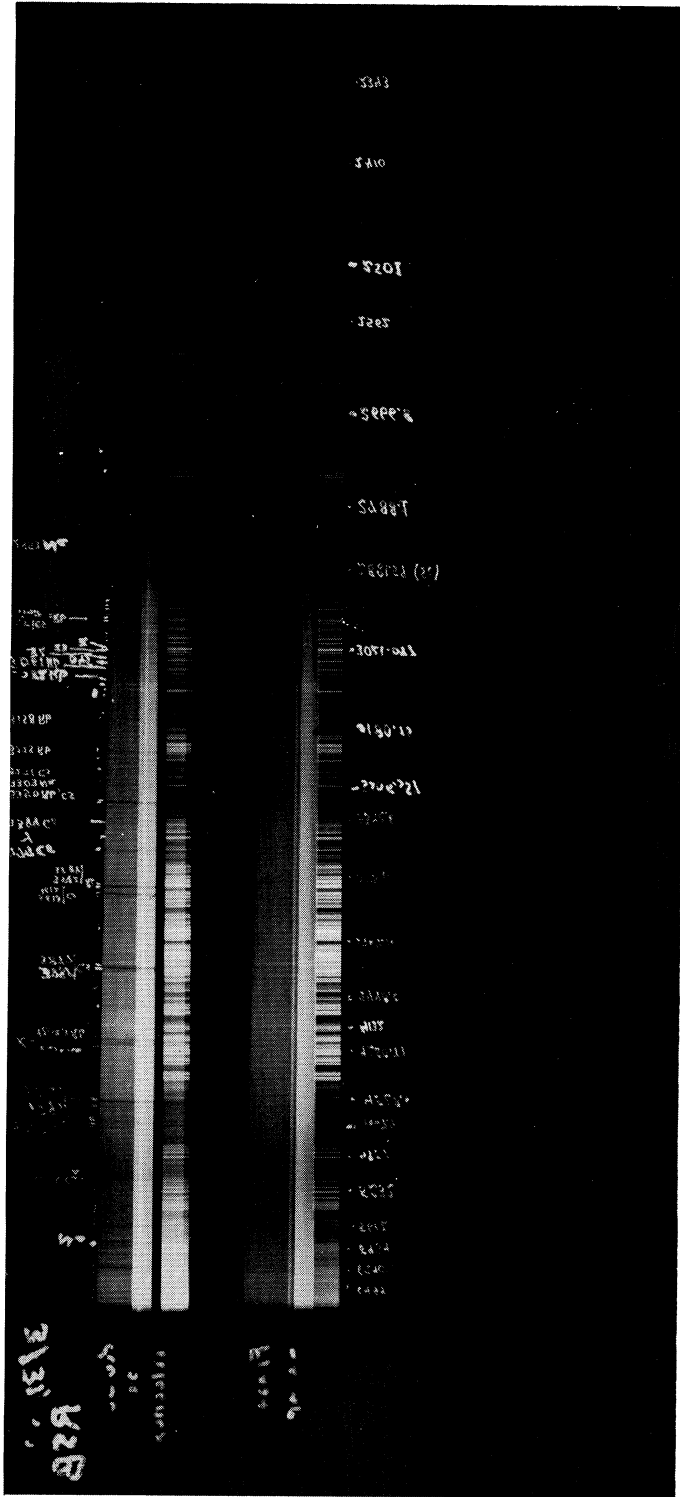
Fig. 4. Absorption Spectrum of Shocked RbCl.
Top: sample
Bottom: comparison
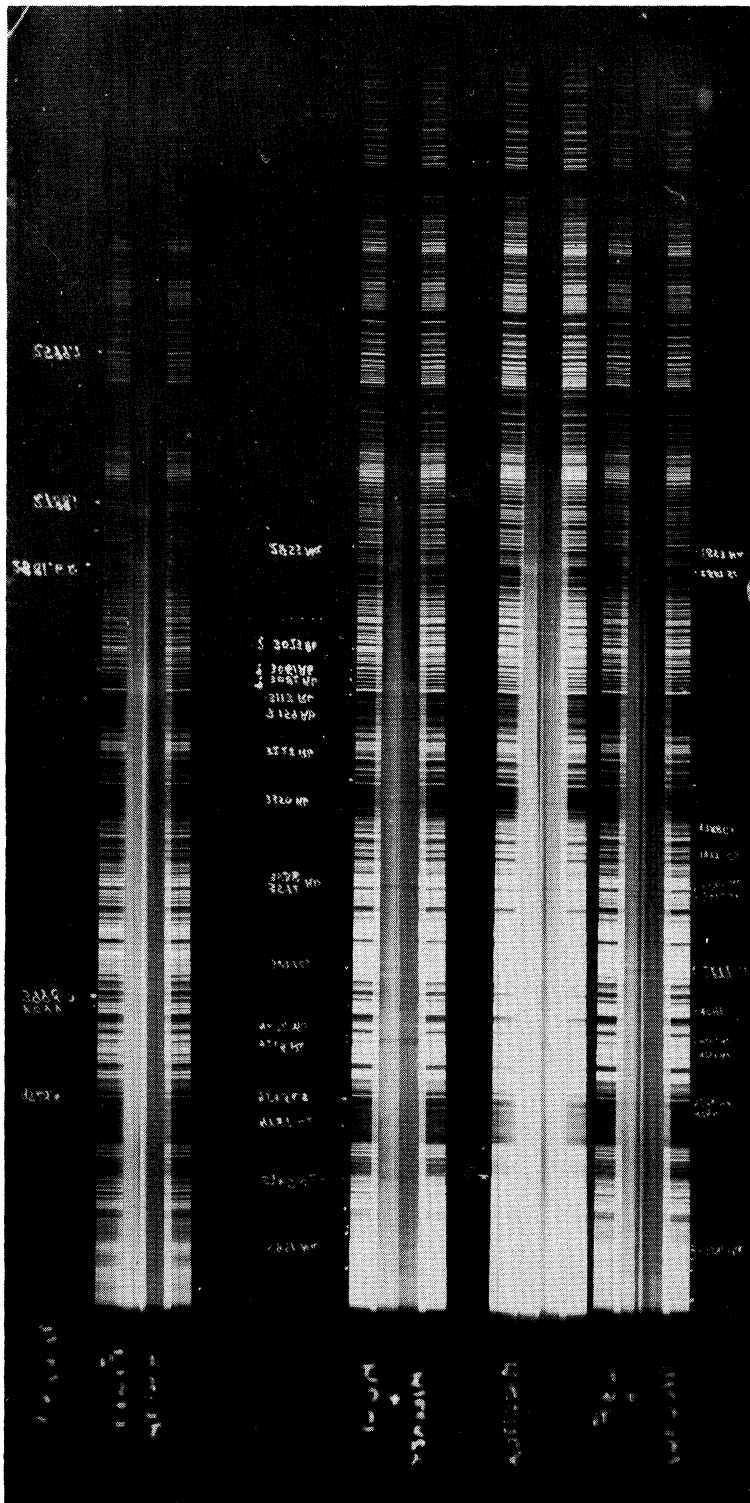
Fig. 5. Absorption Spectra of Shocked RbCl, Cleansing Tissue and CsF. (Note that the shock tube was not cleaned between the shocks shown on this plate.)

1. (Top), flash lamp comparison.
2. RbCl on cleansing tissue.
3. Cleansing tissue alone.
4. CsF on cleansing tissue.

Note the intense C_2 Swan bands, particularly at 5165 and 4737A in the RbCl spectrum.
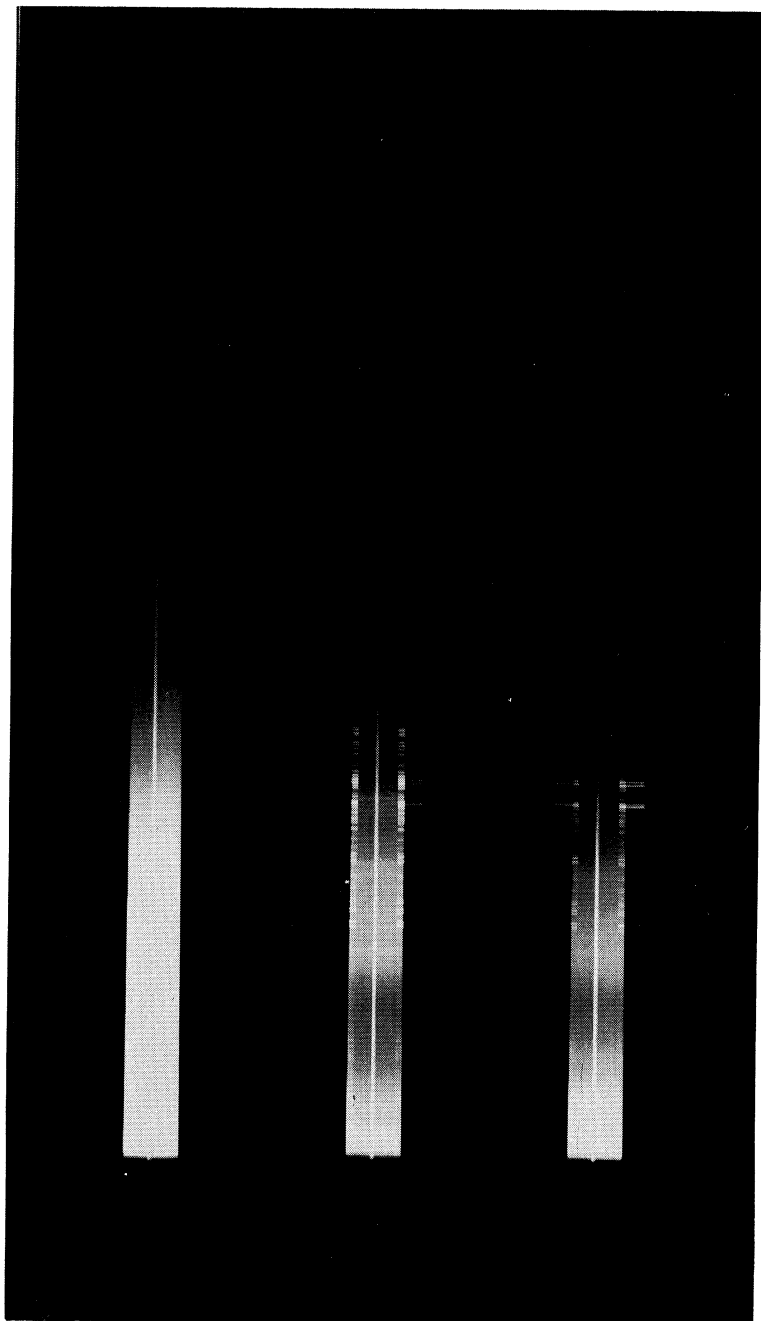
Fig. 6. Possible Onset of "Polyatomic" Band in Shocked B_2H_6. (Top and bottom are comparisons before and after shock.)
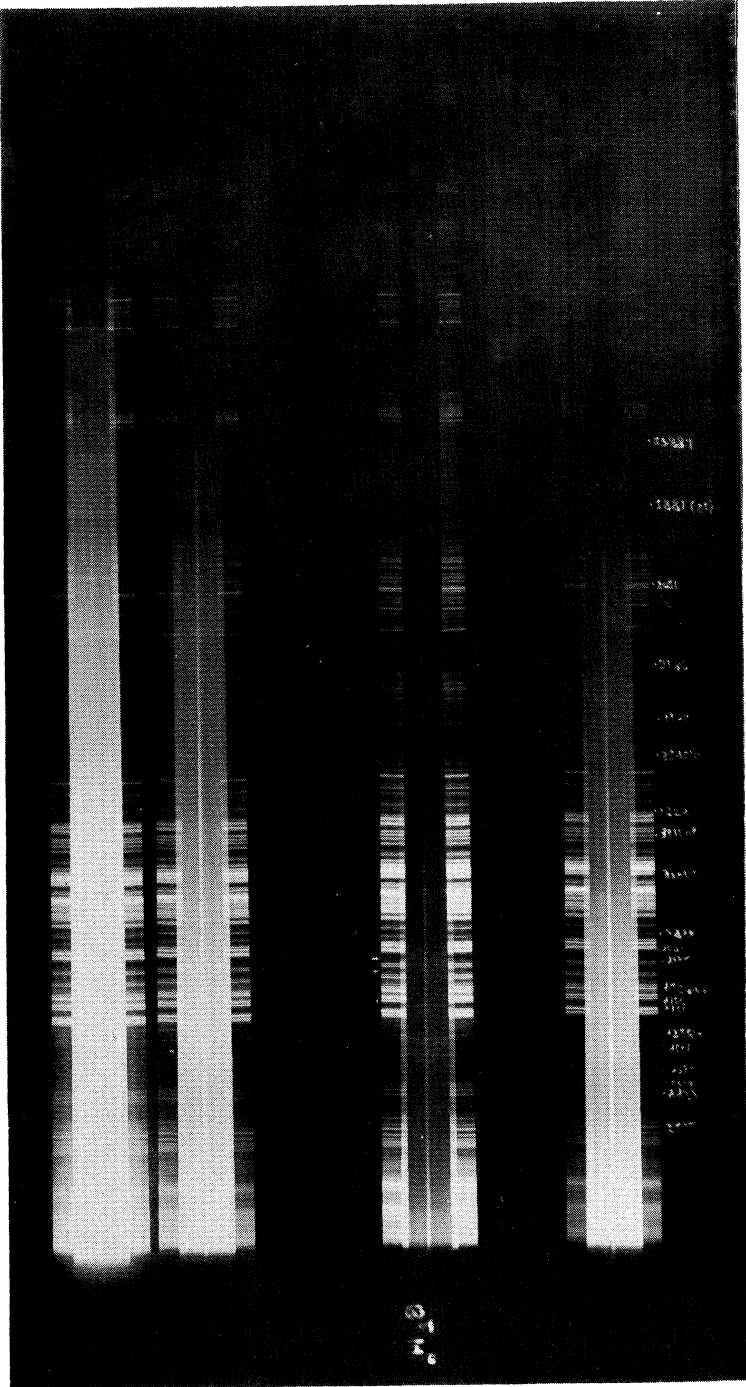
Fig. 7. Further Development of "Polyatomic" Band System.
(Plate also shows possible BH absorption.)
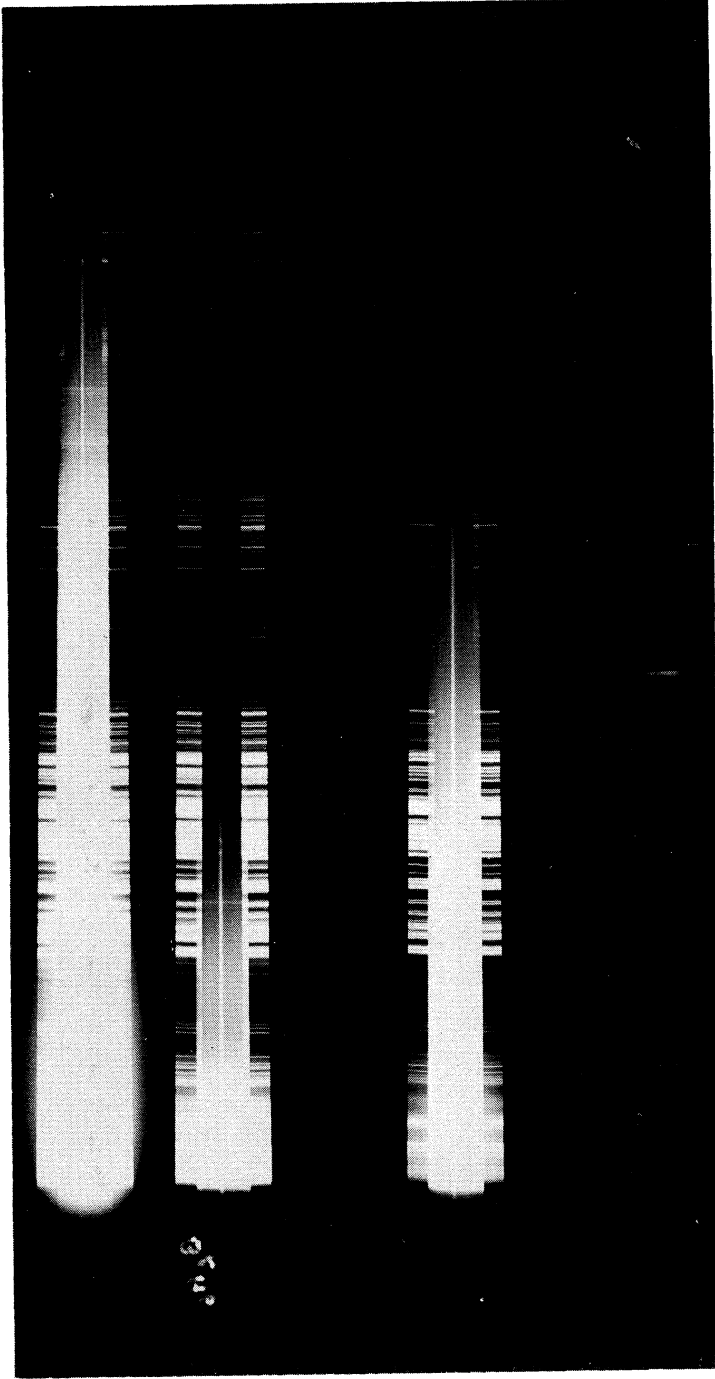
Fig. 8. Further Development of B_2H_6 Behind Shock,
Showing Strong BH Absorption.
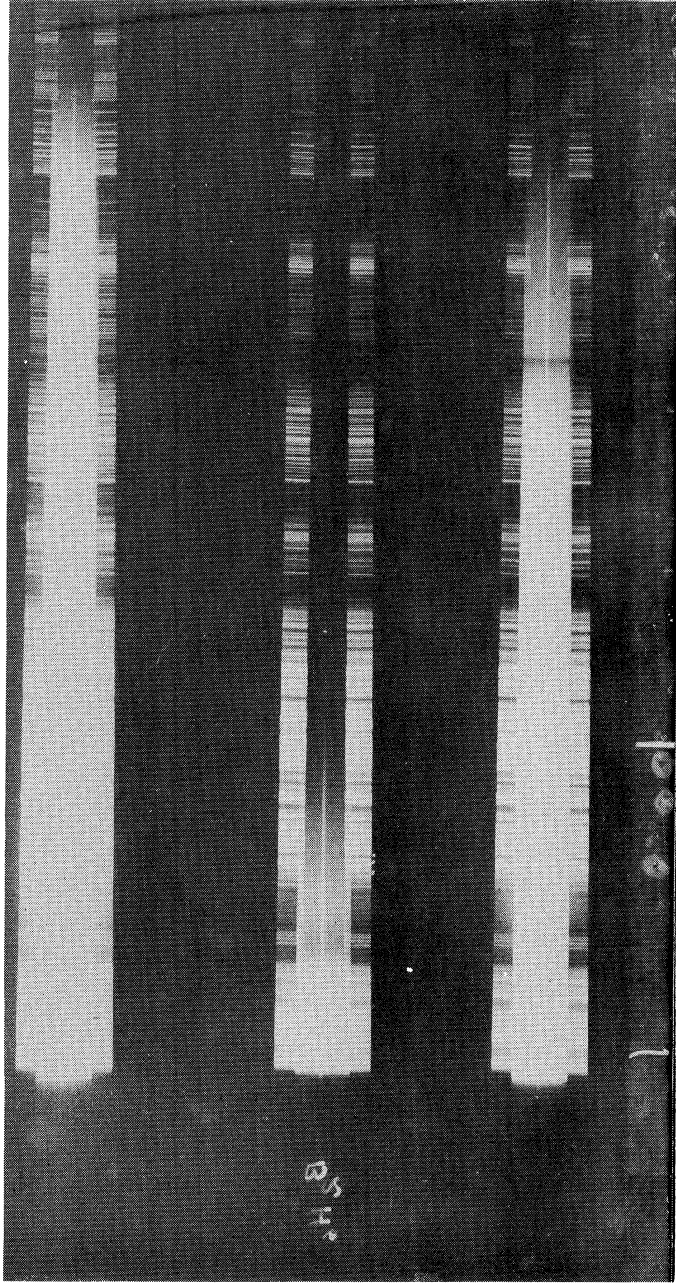
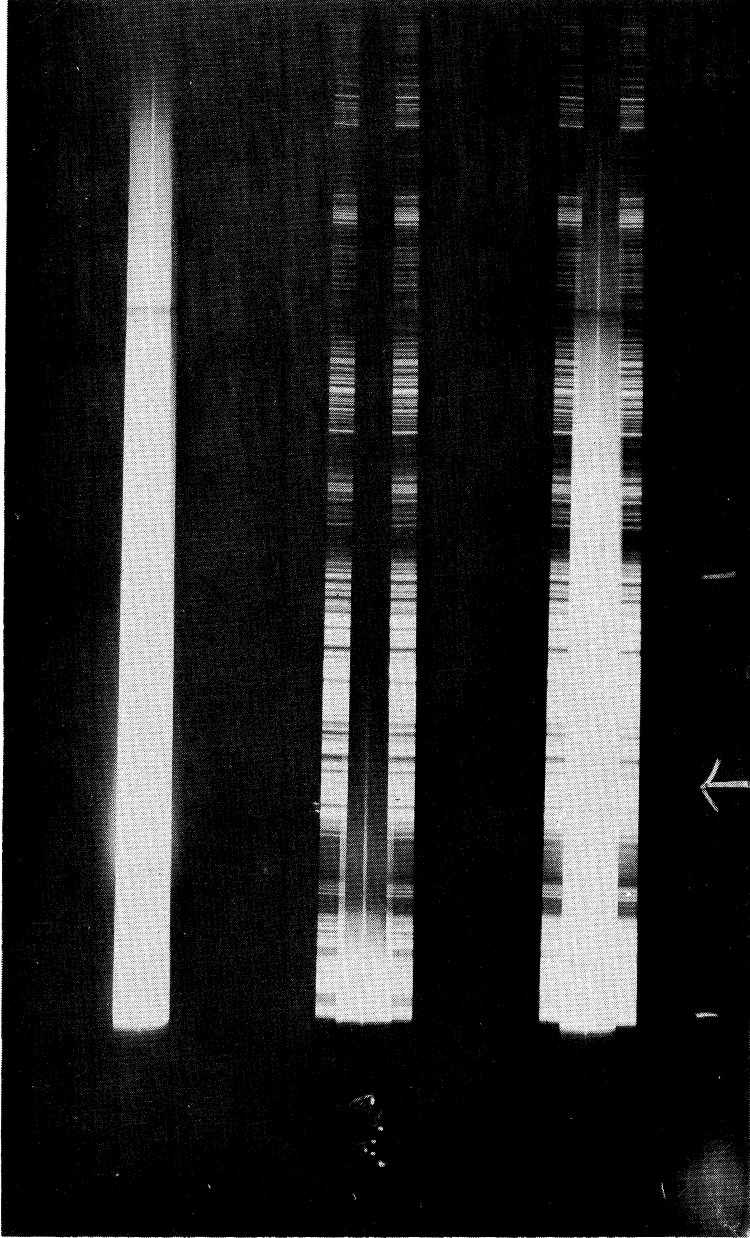Fig. 9. Shocked B₂H₆, Showing 0-0, 1-1, and 2-2
Band Heads of BH.

Fig. 10. B₂H₆ Spectrum Prior to Onset of Total Absorption.

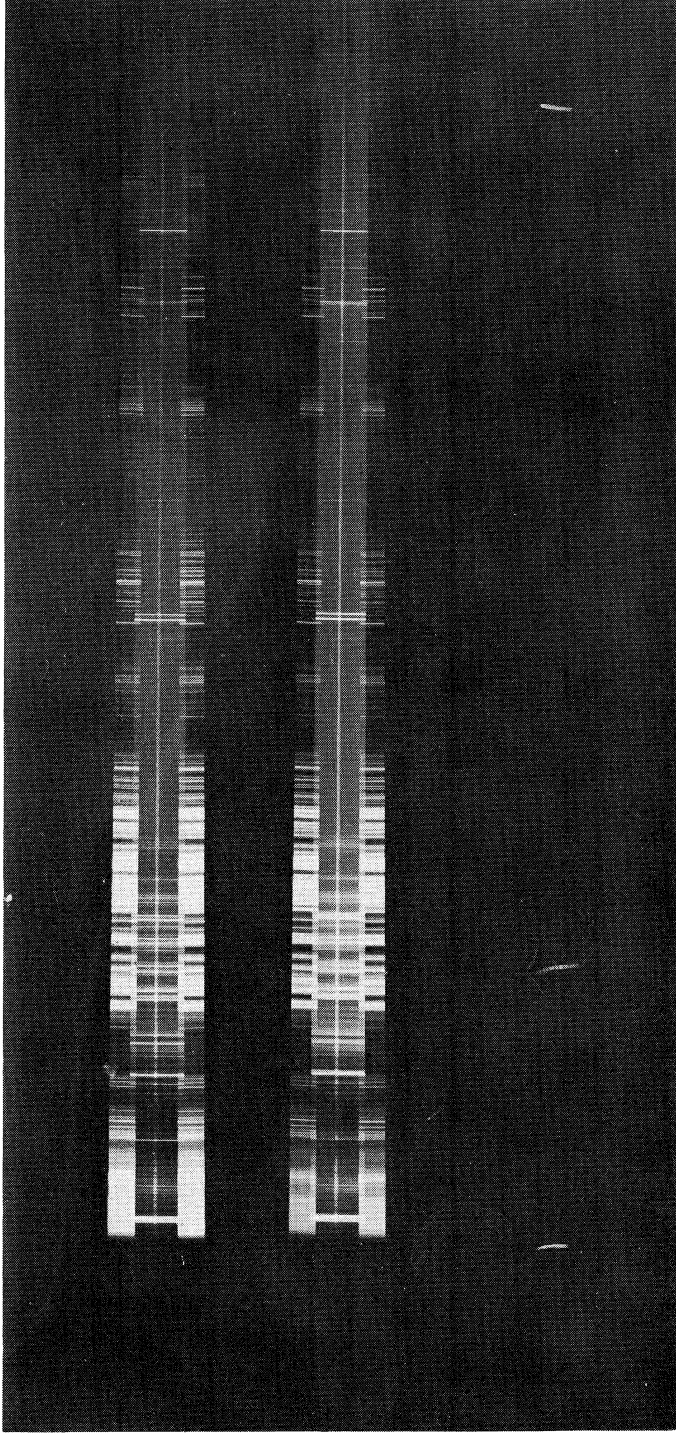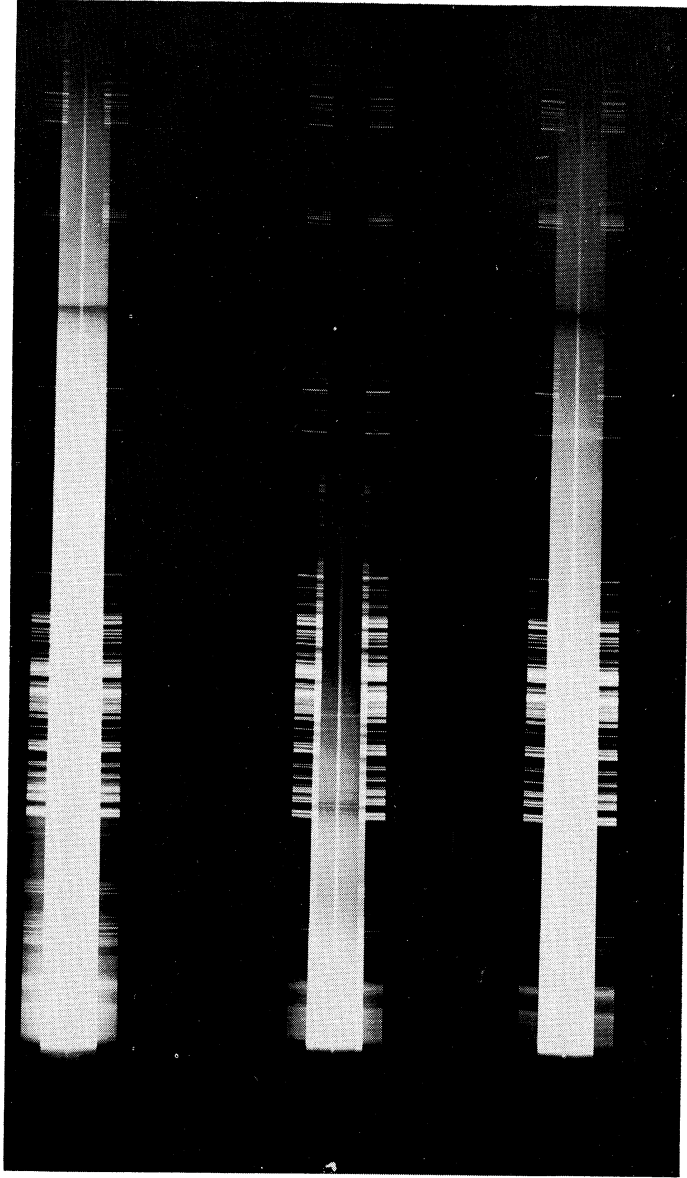Fig. 11. Emission Spectra from Hollow Cathode Lamp Containing BCl_3 + H_2.

Fig. 12. Absorption Spectrum of Shocked B_2D_6, Showing BD Bands.