

Spectroscopic Investigation of Discharges at High Gas Pressure

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Spectra of high energy capacity discharges between electrodes of various metals in N_2 , H_2 , O_2 and He at pressures up to 15 atmospheres have been examined at high dispersion. With the ever-present continuous spectrum as a background, absorption bands due to AlH, MgH, BeO, etc., are observed. The lines of the (0,0) ${}^1\Pi \rightarrow {}^1\Sigma$ AlH band at 4260Å which are not affected by predissociation ($J < 22$) are all uniformly shifted to the red (0.05 cm^{-1} per atmos.) and symmetrically broadened (half-width 0.24 cm^{-1} per atmos.) by about the same amount as for the pressure

effect of H_2 on $S-P$ resonance lines. $\Sigma \rightarrow \Sigma$ bands (CN, BeO) exhibit but slight pressure effects; BeO ${}^1\Sigma \rightarrow {}^1\Sigma$ band lines are shifted 0.033 cm^{-1} to the red per atmos. of O_2 , with no dependence on K . Details of the pressure broadening of the Al resonance lines are presented. The breadths and shifts of the emission lines are attributed principally to interatomic Stark effect plus slight resonance broadening, while the contours and pressure shifts of the self-reversals are about those expected if due to van der Waals forces between Al atoms and gas molecules.

PROMINENT features of the spectra of intense spark discharges in gases at high pressure are the considerable breadth of most of the atomic lines, the self-reversal of those lines involving low-lying energy states, and a continuous spectrum which increases markedly in strength as the gas pressure is raised. Those lines involving transitions between hydrogen-like orbits and consequently showing a first-order Stark effect exhibit the greatest breadths. For example, the close doublet of Mg II at 4481Å, which is a $3d^2D - 4f^2F$ transition, we observe to be broadened symmetrically into a band over 40Å wide when produced in a high energy capacity discharge in hydrogen at 1.3 atmosphere pressure. It has long been known that as the gas pressure in the source is raised, many of the atomic lines are also shifted in wave-length, mostly to the red, and it is now generally believed that interatomic Stark effects are largely responsible for these pressure phenomena. The experiments of Lawrence and Dunnington¹ have shown that the strong continuous spectrum is associated with the initial electron avalanche in the spark breakdown, while Finkelnburg² has assembled the evidence for believing that the continuous spectra in these and all other high current density light sources are electron radiation (recombination spectra plus electron transitions in the regions of positive continuous energy).

An investigation of the broadening of the

Balmer lines of hydrogen and their merging into an intense continuous spectrum as the pressure of the hydrogen atmosphere in the spark chamber is increased from 1 to 30 atmospheres has been made by Finkelnburg.³ When using Al electrodes the ${}^1\Pi \rightarrow {}^1\Sigma$ band system of AlH in the violet was observed in absorption against the continuous background. In a similar manner we have produced in addition to these bands the spectra of several other diatomic molecules in order to determine the exact nature of the pressure effect of foreign gases on electronic band spectra. Finkelnburg's study of the behavior of the Cu resonance lines with increasing H_2 pressure was apparently made with rather low dispersion and with insufficient magnification for the photometer traces to bring out the causes of the pressure broadening phenomena involved. We have therefore photographed and photometered resonance lines of several metallic elements produced by high energy capacity discharges in H_2 , N_2 and He gas up to 16 atmospheres pressure with large enough dispersion and magnification to reveal the details of the pressure effects. There results the conclusion that interatomic Stark effect is the major factor in producing the shift of the maximum and the broadening for the emission lines, whereas van der Waals forces between the gas molecules and the metal atoms are responsible for the pressure broadening and shifting of the self-reversals. We present below a brief report of experiments with the Al resonance lines as a typical example.

¹ E. O. Lawrence and F. G. Dunnington, *Phys. Rev.* **35**, 396 (1930).

² W. Finkelnburg, *Zeits. f. Physik* **88**, 768 (1934).

³ W. Finkelnburg, *Zeits. f. Physik* **70**, 375 (1931).

EXPERIMENTAL PROCEDURE

The spark discharges were made in a pressure chamber constructed of a one-foot length of steel pipe with one inch inside diameter and 5/16-inch wall. Electrode holders extended in from each end through insulating bushings carried in large nuts threaded on to the pipe. A very short side arm at the center of the tube carried a Pyrex glass window one cm thick under another large threaded nut. The bearing surfaces under these nuts were made pressure-tight by means of lead gaskets. Electrodes of Cu, Al, C, Mg, In and Be usually about 8 mm in diameter and somewhat rounded at the tips were set in every case so that the spark gap was about 1 mm in length. H₂, N₂, O₂ and He gas from commercial cylinders was admitted through a high pressure valve. Pressures were read with a gauge carried on a side tube. Although the highest pressure used in these experiments was 16 atmospheres, the pressure chamber could easily be used at pressures several times this amount.

A d.c. voltage varying between 5000 and 20,000 volts just sufficient to break down the gap was used at each pressure. An auto-transformer gave the voltage adjustment by controlling the potential applied to a high voltage x-ray transformer. The secondary of the latter was connected through a kenetron to an 0.25 mf G. E. Pyranol condenser, the number of discharges of the condenser per second being regulated by means of a rotary spark gap in series with the gap in the pressure chamber. Usually the discharges were produced at the rate of two per second, the exposure times varying from 30 minutes at 1 atmos. to 4 minutes at 15 atmos. As the gas pressure was raised, the breakdown voltage increased and the light became whiter and more intense.

All spectrograms were taken in the second order of the 21-foot grating in a stigmatic mounting, the dispersion being about 2.4 Å/mm. Intensity calibration marks were placed on each plate by means of a step filter mounted in front of the slit of the spectrograph. Little use was made of these blackening strips, however, since the uncorrected photometer curves yielded measurements of sufficient accuracy in view of some unavoidable uncertainty in our knowledge of the exact density of the perturbing gas in the

region of the sparking. Photometer traces of all spectrograms were made with the 40 : 1 magnification of the Koch-Goos registering microphotometer.

PRESSURE EFFECT OF FOREIGN GASES ON BAND SPECTRA

This source forms a very convenient method of producing absorption spectra of many diatomic molecules, with of course a small pressure broadening and shift for the lines of the bands in some cases, since 3 or 4 atmos. of gas pressure must be used. We have in this way photographed the AlH bands perturbed by H₂, BeO bands by O₂, CN bands by N₂ and MgH bands by H₂, and have studied details of the pressure effect in the first two. The ²Σ→²Σ violet system of CN as produced in these intense capacity discharges between graphite electrodes persist as emission bands with quite sharp lines for all rotational levels of the lower vibrational states up to N₂ pressures of 16 atmos. Only at the accumulation of lines at the heads of the bands is absorption evident at the highest pressure. No doubt the nonoccurrence of the CN bands in absorption is due to the strong tendency for the CN molecules to combine into the stable chemical forms before diffusion into the absorption region surrounding the discharge can take place.

Spectrograms of the ¹Π→¹Σ AlH (0,0) band at 4260Å in absorption at H₂ pressures of 5.7, 10.7 and 14.7 atmos. have been photometered in the interval between the Q(6) and P(22) lines. One of these microphotometer traces for the range Q(6) to Q(15) is reproduced in Fig. 1. The symmetrical contours are characteristic of hydrogen broadened lines.⁴ Since lines having J > 22 in this band become very diffuse and broad due to predissociation,⁵ the frequencies of the maxima of all single P and Q branch lines with J < 22 only were

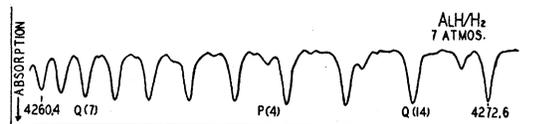


FIG. 1. Microphotometer trace of absorption lines of the 4260Å AlH band broadened by 7 atmos. H₂ pressure.

⁴ H. Margenau and W. W. Watson, Rev. Mod. Phys. 8, 22 (1936).

⁵ E. Bengtsson and R. Rydberg, Zeits. f. Physik 59, 540 (1930).

TABLE I. Pressure shifts ν_0 and half-widths $\nu_{1/2}$ per atmos. of H_2 (cm^{-1} units).

LINES	ν_0	$\nu_{1/2}$	$\nu_{1/2}/\nu_0$
Hg 2537A	0.064	0.41	6.3
Na $\left\{ \begin{array}{l} 5890A \\ 5896A \end{array} \right.$	0.148	0.65	4.3
AlH	0.051	0.24	4.7

measured on the photometer traces by interpolation between Fe lines. With increasing H_2 pressure these frequencies are all shifted to the red by the same amount, the shifts being proportional to the pressure and with no evident variation with the rotational quantum number J . The mean value of this pressure shift to the red for all the lines is $0.051 \text{ cm}^{-1} \pm 50$ percent per atmos., the large possible error arising from the smallness of the wave-length shift ($< 0.01A$ per atmos.). All of these lines for any one H_2 pressure have the same half-value width, this width increasing linearly with the pressure at a rate of $0.24 \pm 0.03 \text{ cm}^{-1}$ per atmos.

A comparison of these pressure effects for AlH band lines with the corresponding shifts and widths of the Hg and Na resonance lines perturbed by H_2 is made in Table I. It is apparent that these values, as well as that for the ratio of half-width to shift, for AlH differ but little from those for these $S-P$ atomic transitions. This is in agreement with the theoretical considerations of Margenau.⁶ The nonvariation of the pressure effects with molecular rotation is also in accordance with the theory.

An estimate of the pressure shift produced by O_2 on the lines of the $(0,0) \ ^1\Sigma \rightarrow \ ^1\Sigma$ band of BeO at 4709A has been made by photometering the lines $P(12)$ to $P(16)$ and $R(53)$ to $R(57)$ on an absorption spectrogram taken at 7 atmos. O_2 pressure, measuring the wave-lengths of the line maxima on this photometer trace, and comparing with the wave-lengths similarly determined for this band as developed in emission in air at atmospheric pressure. The absorption lines are all shifted to the red of the corresponding emission lines, the average shift being 0.196 cm^{-1} with no dependence on the rotational state detectable. If the pressure difference between these two spectrograms is 6 atmos., the pressure shift per atmos. is thus about 0.033 cm^{-1} . The pressure

⁶ H. Margenau, this issue.

shift of the Hg 2537A line produced by O_2 is 0.123 cm^{-1} per atmos., the smaller value for these BeO band lines being possibly due to the fact that both of the electronic states have closed shell configurations (Σ states). In this connection it may be noted that the pressure insensitive CN bands are also a transition between Σ states.

PRESSURE EFFECT FOR THE Al RESONANCE LINES

Fig. 2 is a comparison of microphotometer traces of the $3p \ ^2P_{1/2} - 4s \ ^2S$ resonance line of AlI at 3961A as developed in these capacity discharges between Al electrodes in H_2 and N_2 , both at 2.9 atmos. pressure. In Fig. 3 the intensity distribution through the same line is shown for H_2 and N_2 pressures of 8.7 atmos. At the lower pressure one notices at once that both the emission lines and the self-reversals have fairly symmetrical contours, that the emission line is considerably broader than the absorption line, and that the intensity maximum of the emission line is markedly shifted to the red. At the higher pressure the very broad emission lines have become partially fused with the strong continuous spectrum, and the lines are virtually just broad absorption lines against an approximately continuous background.

The maxima of the self-reversals are also shifted to the red by increase of H_2 or N_2 pressure. Measurement of these absorption maxima on the H_2 -broadened line by reference to the He lines shows a shift of 0.072A for the 8.7 atmos. pressure as compared to the wave-length at 2.9 atmos. This represents a shift of 0.08 cm^{-1} per atmos. which from Table I is seen to be an average pressure shift for H_2 -broadened resonance lines. The corresponding figure for the self-reversals of the N_2 -broadened line as shown in Figs. 2 and 3 is 0.043 cm^{-1} red shift per atmos. From these data, together with the estimates of the half-widths, one concludes that the pressure effect of the self-reversals is entirely due to forces of the van der Waals type between the absorbing Al atoms in the cooler regions surrounding the discharge and the perturbing foreign gas molecules. Certainly the reversals are not sharp absorption lines as reported by Finkelburg.³ Humphreys⁷ some years ago, using different

⁷ W. J. Humphreys, *Astrophys. J.* **26**, 18 (1907).

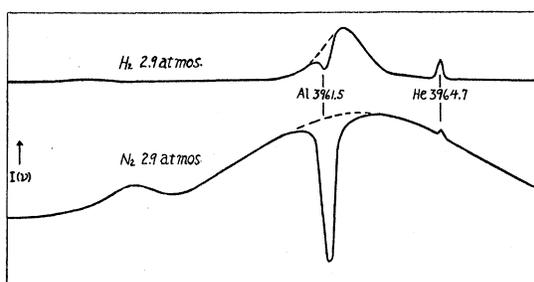


FIG. 2. Comparison of microphotometer traces of the Al I resonance line at 3961 Å broadened by H₂ and N₂ at 2.9 atmos.

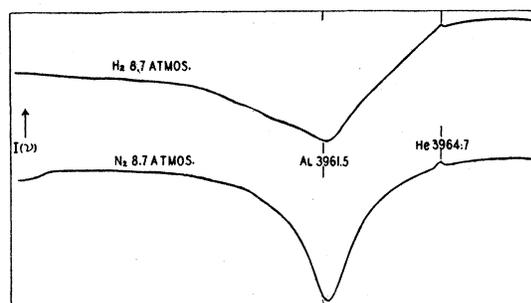


FIG. 3. Photometer traces of the 3961 Å Al line broadened by H₂ and N₂ at 8.7 atmos.

experimental methods, determined the pressure shift of this (self-reversed) Al line for air at 42 atmos. to be 0.180 Å to the red, a value which, per atmos., is in rough agreement with our value of the shift for nitrogen.

For this 3961 Å line broadened by H₂ at 2.9 atmos. pressure shown in Fig. 2 the maximum of the emission line is shifted 0.546 Å or 3.48 cm⁻¹ to the red of its vacuum wave-length. The corresponding shift of the emission maximum for N₂-broadening at the same pressure is 0.750 Å = 4.78 cm⁻¹. Now Ishida and Fukushima⁸ have measured the quadratic Stark effect on this Al line as a shift to the red of 0.5 Å in a field of 500,000 volts/cm. Using Finkelburg's method of estimating the average interatomic electric field strength by noting the disappearance of the higher members of the Balmer series with increasing H₂ pressure in comparison with the Stark effect findings of Rausch v. Trautenberg⁹ on the existence limits of these lines in high fields, we should say that the mean interatomic field in our experiment at 2.9 atmos. H₂ pressure was at least 500,000 volts/cm, since Hγ is barely visible and all higher series members have disappeared. It would thus seem that interatomic Stark effect, with a considerable spread of the effective field about this mean value, is a major factor in broadening and shifting such an emission line in intense sources. Of course, resonance broadening¹⁰ must make some contribution to the line breadth, but rough calculation assuming any reasonable value for the density of Al atoms

indicates a half-width from this source of but a fraction of 1 cm⁻¹. The emission line broadened by H₂ as shown in Fig. 2 has a half-width of about 9 cm⁻¹, with at least 0.8 of the area to the red of the vacuum frequency position.

The approximately 50 percent greater red shift of this Al emission line when N₂ rather than H₂ is used at the same pressure is due to greater ion density and hence greater interatomic fields. For we find that the breakdown potential for the spark gap is about twice as great for N₂ as for H₂ (11,000 volts per mm gap space for N₂ as against 5500 volts per mm for H₂ for these spectra at 2.9 atmos.). There is thus with the N₂ atmosphere a greater ionization in the path of the discharge to produce a larger quadratic Stark effect due to ion fields. If we assume that the density of ions n with N₂ is twice as great as with the H₂, and use the result of the Debye¹¹ and Holtmark¹² theories that the mean interatomic field F should vary as $n^{2/3}$, then $F_{N_2}/F_{H_2} = (2/1)^{2/3} = 1.36$. If the red shift of the maxima of these pressure-broadened emission lines is due to quadratic Stark effect resulting from these fields, we have $(F_{N_2}/F_{H_2})^2 \approx 0.75/0.54$ or $F_{N_2}/F_{H_2} = 1.22$. There is fair agreement between these two values of the ratio of the mean interatomic field strengths.

To produce these high fields of the order of 10⁶ volts/cm there must be a sizable percentage ionization in the spark path. This is understandable in view of the high current density which computation shows must be of the order of 10,000 amperes/cm² in the first half-cycle of the condenser discharge. Transitions between energy states capable of existing in such fields should

⁸ Y. Ishida and M. Fukushima, *Sci. Papers Inst. Phys. and Chem. Res.* **14**, 123 (1930).

⁹ H. Rausch v. Trautenberg, *Physik. Zeits.* **31**, 958 (1930).

¹⁰ Reference 4, §5.

¹¹ P. Debye, *Physik. Zeits.* **20**, 160 (1919).

¹² J. Holtmark, *Physik. Zeits.* **20**, 162 (1919); *Ann. d. Physik* **58**, 577 (1919).

always display some quadratic Stark effect which usually involves a shift of the frequency to longer wave-length. Sometimes, however, this Stark effect shift is to the blue, as, for example, in the 3933A and 3968A doublet of Ca II (the *H*

and *K* lines) for which we observe at any pressure a blue shift of about 1/4 the amount of the red shift of the Al lines.

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PHYSICAL REVIEW

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Note on Pressure Effects in Band Spectra

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A simple theory is presented describing pressure effects on band lines, insofar as they are due to foreign perturbing molecules without permanent polarity. Results are: Band lines are shifted and broadened much in the manner of atomic lines as a result of van der Waals interactions. Calculations with the models of a rigid rotator and a simple harmonic oscillator, for which formulas are given, show that the effects are practically independent of rotational and vibrational quantum numbers.

THE effects of pressure on spectral lines are due, as is well known, to the interactions of the radiating particles with their neighbors. These interactions are of two main types: those which arise between similar systems, and those between dissimilar ones. The former are usually caused by optical resonance (except when both partners are unexcited), i.e., by the fact that a quantum of energy can be exchanged between the two agents in question; the magnitude of the perturbation is then proportional to the oscillator strength (*f* value) corresponding to the resonance transition. The latter type of interaction results from the mutual polarization of the partners; its magnitude depends on the *f* values of all possible transitions of both partners.

The phenomenon of "self-broadening," that is broadening by the same gas which emits or absorbs the line, is to be attributed principally to resonance interactions. It is particularly strong for atomic resonance lines, since their *f* values are large. Band lines, however, cannot be expected to exhibit this effect so markedly. For every electronic state of a molecule has a multiplicity of sublevels capable of combinations. The *f* value, which in the atomic case belonged to a single transition, is divided between several transitions, and the sharpness of resonance is thereby impaired. On the other hand,

the second effect, which is evident in the broadening and displacement of lines by pressures of foreign gases, is of comparable magnitude in atoms and in molecules. It is to this effect that we wish briefly to call attention, since recent experiments by Watson and Hull¹ have yielded some quantitative information regarding it.

When a molecule in a state *k* is subject to the influence of a perturbing gas molecule having no dipole moment, and in its normal state, the system undergoes an energy change which is given by

$$\overline{\Delta E} = -\frac{2}{3R^6} \sum'_{\lambda\kappa} \frac{|(qr)_{0\lambda}|^2 |(qr)_{k\kappa}|^2}{F_\lambda - F_0 + E_\kappa - E_k}, \quad (1)$$

a formula which results from an application of the ordinary perturbation theory. F_0 is the energy of the normal state of the perturber (I), the E 's are the energies of the excited molecule (II), qr denotes the dipole moment associated with a transition. The index λ labels the states of I, κ those of II. R is the distance between the particles, and the bar over ΔE indicates that an average over all orientations of molecule II has been taken. Formula (1) neglects the contribution of multipoles.

Since F_0 denotes the lowest energy of the perturber, all differences $F_\lambda - F_0$ are positive.

¹ W. W. Watson and G. F. Hull, Jr., Phys. Rev., this issue.