

Shock Tube Measurement of Pb I Lines*

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Oscillator strengths of lead atom spectral lines have been measured by observing the radiation emanating from gas samples heated to 10 000 °K in a pressure-driven shock tube. Shocks were produced by allowing hydrogen at high pressure to rapidly expand into dilute mixtures of tetraethyllead and neon. The thermodynamic state of the spectroscopically interesting gas behind the reflected shock was computed by using the measured shock velocity to estimate the state of an ideal gas, then using the state variables so derived to estimate the energy consumed in real gas effects, and completing the cycle by recalculating the state variables. Spectroscopic observations were made with a double prism spectrograph coupled with a revolving drum camera. The Stark broadening of H_{β} was used to measure the electron density of the gas behind the first reflected shock. Quantitative spectroscopic analysis of lead atom emission lines led to the following absorption f -values: $\lambda = 3639$, $f = 0.04$; $\lambda = 3683$, $f = 0.07$; $\lambda = 4057$, $f = 0.15$.

A PRESSURE-driven shock tube has been used as a shock spectroscopic source for the measurement of absolute intensities of Pb I lines at wavelengths 3639, 3683, and 4057 Å. Shocks were produced by allowing hydrogen at high pressure to rapidly expand into neon at pressures of about 8 mm Hg. A shock discontinuity moves with supersonic velocity through the neon to the end wall of the tube, where a reflected shock is initiated, further heating and compressing the gas. Pressure ratios across the primary shock discontinuity were near fifty, corresponding to shock Mach numbers from 6.5 to 7. In order to observe the spectral lines of lead, small amounts of tetraethyllead were added to the neon. The thermodynamic state of the spectroscopically interesting gas behind the reflected shock was computed in the manner described by Wilkerson.¹ Similar calculations are given by Hurle and Gaydon² and Bradley.³ (See also the review of Charatis and Wilkerson.⁴) We used the photographically measured shock velocity to compute state variables on the assumption of ideal gas behavior, then employing the state variables so derived to estimate the energy consumed in real gas effects. The computational cycle was completed by then recalculating the state variables.

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¹ T. W. Wilkerson, Ph.D. thesis, University of Michigan (1961).

² A. G. Gaydon and I. R. Hurle, *The Shock Tube in High Temperature Chemical Physics* (Reinhold Publishing Corporation, New York, 1963).

³ J. N. Bradley, *Shock Waves in Chemistry and Physics* (John Wiley & Sons, Inc., New York, 1962).

⁴ G. Charatis and T. D. Wilkerson, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1963), Vol. 3, p. 401.

FIG. 1. Wave speed diagram.

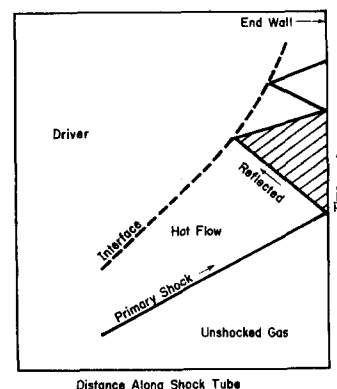


Figure 1 is a wave speed diagram showing the trajectories of primary and reflected shocks in $x - t$ space. The shaded area is the first reflected region.

Because the emission spectra of lead were to be studied, calculations for shocks in tetraethyllead diluted in neon have been made. The concentration of $PbEt_4$ required for useable intensity measurements is quite small, on the order of hundredths of a percent. Nonetheless, one must account for the absorption of thermal energy in the dissociation and ionization of molecules and atoms, for its effect on the temperature of the final state behind a reflected shock is appreciable. Table I gives computed conditions behind reflected shocks of varying strength.

Spectroscopic observations for the purpose of determining absolute line intensities were made with a double prism quartz spectrograph coupled with a rotating drum camera. Spectrographic 35-mm film was mounted in the drum so that the film could be moved parallel to the spectral lines during an exposure to shock tube luminosity, thus providing a time-resolved spectrogram. It was then possible to examine only the emission from the region behind the first reflected shock. The time during which

TABLE I. Conditions behind reflected shocks. The shock strength, τ_0 , is defined as $\tau_0 = \sigma_0 U^2 / RT_0$, where σ_0 is the mean molecular weight and T_0 the temperature of the unshocked gas. R is the gas constant and U the primary shock speed. In all cases $T_0 = 300^\circ\text{K}$, initial pressure was 1.03×10^4 dyn/cm² and the molar concentration of PbEt₄ in neon taken as 3×10^{-4} .

| Shock Strength τ_0 | Temp. T °K | Reduction from Ideal Gas Temp. ($T^0 - T$) | Degree of Ionization | | | Electron Density n_e |
|----------------------------|-----------------|---|--|---------|--------------------|---------------------------|
| | | | $\alpha = \frac{N_{\text{ion}}}{N_{\text{atom}} + N_{\text{ion}}}$ | | | |
| | | | Pb I | C I | H | |
| 30 | 4170 | 28 | 0.073 | | | |
| 40 | 5455 | 87 | 0.52 | 0.00014 | 9×10^{-7} | 3.3×10^{14} |
| 50 | 6674 | 219 | 0.924 | 0.0079 | 8×10^{-5} | 6.2×10^{14} |
| 65 | 8577 | 346 | 0.987 | 0.213 | 0.0091 | 2×10^{15} |
| 80 | 10 426 | 517 | 0.9932 | 0.663 | 0.104 | 6.4×10^{15} |
| 90 | 11 500 | 775 | 0.9949 | 0.838 | 0.229 | 1.2×10^{16} |

useful observations can be made in this region is approximately 200 μsec at a point 3 cm upstream from the end wall of the shock tube.

The manner in which oscillator strength data is derived from intensity measurements is well established. Let us consider the intensity in the neighborhood of an isolated spectral line produced by a homogeneous source of thickness l . If I_ν is the energy radiated by the surface of the source per unit time, area, and solid angle, in the frequency interval $(\nu) \rightarrow (\nu + d\nu)$, then, where there are no other sources,

$$I_\nu = B(\nu, T)[1 - \exp(-\kappa'_\nu l)]. \quad (1)$$

Here $B(\nu, T)$ is the Planck blackbody function $2h\nu^3/[c^2(e^{h\nu/kT} - 1)]$ and $\kappa'_\nu = [1 - \exp(-h\nu/kT)]\kappa_\nu$, is the absorption coefficient corrected for stimulated emission. The uncorrected absorption coefficient may be expressed in terms of the absorption oscillator strength, f_{ij} , by

$$\kappa_\nu = (\pi e^2/mc)n_i f_{ij} P(\nu), \quad (2)$$

where n_i is the number of atoms in the lower electronic state and $P(\nu)$ is a line shape function whose integral over the frequency is normalized to unity. The solution to the equation of radiative transfer given in Eq. (1) is valid where the populations of the atomic energy levels are in equilibrium at temperature T , and thus related by the Boltzmann factor.

The product $\kappa'_\nu l$ is called the optical depth of the radiating sample. If it is much smaller than unity, we have an optically thin source and can expand the exponential in (1) to obtain

$$I_\nu = \kappa'_\nu l B(\nu, T), \quad (3)$$

which is easily integrated over the frequency interval containing an emission line to yield

$$I = \int I_\nu d\nu = \frac{2\pi h e^2}{m} \frac{n_i l}{\lambda^3} (gf), \quad (4)$$

where n_i is the number density of atoms in the upper state of the transition of central wavelength λ . Most of the oscillator strength data reported below was derived from observation of optically thin lines. In cases where this was not possible, the curve of growth⁵ method was used to account for absorption.

Measurement of the absolute intensity of frequency integrated spectral lines is accomplished with the use of an entrance slit sufficiently wide to give a flat top to a densitometer trace of the spectrographic emulsion. The density of the integrated line is compared, via the techniques of heterochromatic photometry, with that produced by a radiation standard.

We do this by first arranging the external optics of the spectrograph in such a way that they accept radiation from identical areas and solid angles of both shock tube and carbon arc. Thus we need only compare the output power per unit frequency interval of the standard and unknown sources. Now the photographic emulsion responds to incident light by darkening; if E is the exposure, or product of radiant power and time, and T the transmission of the film, then we may write formally $T = f(\nu, E)$ to express the fact that the response of the emulsion varies with frequency of incident radiation. For each frequency at which we need intensity information from shock-tube radiation, a separate analysis of the dependence of T on E must be made. Moreover, because the emulsions vary from lot to lot, and with storage and development technique, one must be careful to standardize their treatment in order to insure reproducibility.

The first step in the analysis is the recording of

⁵ J. S. Penner and R. W. Kavanagh, J. Opt. Soc. Am. **43**, 385 (1953).

photographic density of the lines in the spectrum (assuming the lines have been identified). To do this, we employ a recording microdensitometer. This device measures the light transmitted by the film with a photomultiplier whose signal is logarithmically amplified and fed to a recording potentiometer. The film holder may be driven across the field of the microscope objective with great precision. If we let i_0 denote the intensity of light transmitted by the clear portion of the spectrographic film and i_1 the intensity transmitted by a spectral line, then its photographic density is defined to be $d = \log_{10} i_0/i_1$. Thus, a faint line will have a density approaching zero because $i_0 \approx i_1$, while a strong line where $i_1 \ll i_0$, will have density which can be greater than unity.

Having found the density of the spectral line, we must convert it to a relative exposure. This conversion is made by constructing the well-known H and D curve for the photographic emulsion; that is, a plot of density versus log exposure. Now, the density is a measure of the response of the film which, in turn, is proportional to the product of intensity and time—the exposure. To determine the relation empirically as a function of wavelength, we expose a film in a spectrograph using a xenon flash lamp which provides good continuum illumination and allows short exposure times. It is, of course, important to calibrate the film with exposure times comparable to those with which shock-tube spectra are made to avoid “reciprocity law” failure in the emulsion. [This failure is in evidence when, for example, the exposure $E_1 = I_1 \times t_1$ resulting from illumination of the film with intensity I_1 for time t_1 is not equal to $E_2 = (\frac{1}{2}I_1) \times (2t_1)$, resulting from half the intensity and twice the exposure time.] We achieve a range of exposure by placing a neutral density-step filter in front of the spectrograph slit. By adjusting the entrance slit of the spectrograph, or using a number of flashes of the xenon lamp, one can extend the range of coverage of one’s empirical relation between exposure and density. The usual technique for displaying this relation is a plot of log exposure versus density, d . This curve is frequently linear in the middle of the density range of the emulsion, but often departs from linearity toward the lower densities. Since the spectral line densities in time resolved shock tube exposures are often quite low, it is convenient to use a transformation of the density scale that provides linearity at low densities. The Seidel function, $S = \log_{10} [10^d - 1]$, is such a transformation and a plot of log exposure versus S is usually linear over a wide range of den-

sity. [The Seidel function is defined by letting $S = \log_{10} (1 - T)/T$ where T is the transmission of the film; thus, $\lim_{T \rightarrow 1} S = -\infty$, whereas since $d = \log_{10} T^{-1}$, we get $\lim_{T \rightarrow 1} d = 0$.] If one finds a linear relation between S and log exposure, one is saved the trouble of constantly converting densities to relative exposures graphically. The slope of such a line will vary with wavelength, and it is convenient to plot $R(\lambda)$ versus λ , where $S = R(\lambda) \times \log \text{ exposure}$.

Calibration of the emulsion is completed by fixing the relative exposure scale found above to a known absolute radiation standard. Here, we have used the results of Euler on the carbon arc.⁶

If one observes the anode crater of a carbon arc lamp, the radiant energy spectrum is that of a black body at $3995^\circ \pm 20^\circ\text{K}$ with emissivity varying with wavelength (but roughly equal to 0.75). By observing the radiation standard (carbon arc) with the same spectrograph and external optics as used for shock-tube exposures, we effectively cancel out all absorbing and scattering by the optics. The film on which the arc spectrum is recorded is then traced with the microdensitometer and the densities converted to S values using, again, $S = \log_{10} (10^d - 1)$. The exposure of the carbon arc is made with the rotating drum film holder, as for shock-tube spectroscopy. A shutter is placed in the optical path to insure that no more than one revolution of the drum is made during the exposure. The time of exposure for any point on the film is simply the height of the image of the spectrograph slit divided by the linear speed of the film at the focal plane: i.e., $\Delta t^{\text{arc}} = h^{\text{arc}}/\pi DW^{\text{arc}}$, where D is the film drum diameter, W the speed of rotation of the drum during the arc exposure in revolutions per second, say, and h^{arc} the height of the slit for the carbon arc exposure. Once again, to avoid reciprocity law failure, it is important to have $\Delta t^{\text{arc}} \approx \Delta t^{\text{line}}$, where Δt^{line} is the exposure time for a spectral line in a shock-tube experiment.

We may now determine the absolute intensity of a spectral line observed in shock-tube emission. Assuming that we have employed a wide entrance slit so that the exposure is proportional to the frequency integrated line intensity, we write

$$I^{\text{line}} = \int_0^\infty I_\nu d_\nu = \frac{E^{\text{line}} \Delta t^{\text{arc}} \Delta \nu^{\text{arc}}}{E^{\text{arc}} \Delta t^{\text{line}}} \epsilon_\nu B(\nu T_0),$$

where the ratio of exposure of line and arc is found by setting

$$\log \frac{E^{\text{line}}}{E^{\text{arc}}} = R^{-1}(\lambda) \{S^{\text{line}} - S^{\text{arc}}\}.$$

⁶ J. Euler, Ann. Physik 11, 203 (1953); 14, 10 (1954).

The quantity $R(\lambda)$ is the slope of the S versus \log exposure plot for the wavelength λ . The ratio of exposure times is simply

$$\frac{\Delta t^{\text{arc}}}{\Delta t^{\text{line}}} = \frac{h^{\text{arc}}}{h^{\text{line}}} \times \frac{W^{\text{line}}}{W^{\text{arc}}}.$$

The quantity $\epsilon_{\nu} B(\nu, T_0)$ is the product of arc emissivity and Planck functions for frequency ν and temperature $T_0 = 3995^{\circ}\text{K}$. Since the carbon arc provides a continuum source, each point on the spectral film is illuminated by light from a range of frequencies $\Delta\nu^{\text{arc}}$ defined by the width of the image of the slit multiplied by the reciprocal dispersion of spectrometer at the wavelength in question.

We add here a practical note on the establishment of a density scale in tracing the photographic emulsion. Although photographic density is defined to be $d = -\log_{10} T$, where T is the transmission of the image, it is not always possible to obtain a linear photo detector (or photomultiplier) and a strictly logarithmic amplifier for one's microdensitometry. We have found it convenient to define the density scale with a set of Eastman Kodak neutral density filters, graded in steps of 0.1 from 0.1 to 1.0. It is not important that these nominal densities be precisely related to the transmittance of the filter as long as the same set is used to calibrate the microdensitometer's response for each piece of film that is traced.

A spectroscopic probe was employed to verify theoretical predictions of the state of the gas behind the reflected shock. The Stark broadening of H_{β} was observed and used as a measure of the electron density.⁷ Although hydrogen was present in the shock heated gas by virtue of its presence in the $\text{Pb}(\text{C}_2\text{H}_5)_4$ molecule, the intensity of H_{β} emission was insufficient to be recorded with the moving film spectrograph in the same experiments where useful intensities of Pb I lines were emitted. Recourse was made to photoelectric detection, using a device designed to measure the shape and total intensity of H_{β} as a function of time. (The principle of operation of this device is described elsewhere.⁸) The detector was placed in the focal plane of a grating spectrometer aligned to observe the point in the gas seen by rotating drum spectrograph.

Measured electron densities were about 20% lower than predicted by equilibrium thermodynamics. The deficiency can be attributed to the incomplete ioniza-

tion of the neon. Although the equilibrium degree of ionization of neon at temperatures and pressures of our experiments was small ($\alpha \simeq 10^{-4}$), about 30% of the equilibrium electron density is contributed by this atom. The calculated state variables for the gas behind the reflected shock were altered to fit the observed electron density. This alteration was in the direction of higher temperature since less energy was assumed to have been absorbed in ionizing neon.

Tetraethyllead ($\text{Pb}[\text{C}_2\text{H}_5]_4$ or PbEt_4) was chosen as a convenient lead bearing compound for use in the shock tube because its vapor pressure at or below room temperature was sufficient to prepare a useful mixture with neon. Because knowledge of the amount of PbEt_4 in the shock tube was crucial to quantitative measurement of atomic transition probabilities, a brief discussion of the procedure used in introducing it into the tube follows. Liquid PbEt_4 , obtained in fairly pure form from the Ethyl Corporation, was placed in a small vacuum flask connected to a 22-liter mixing flask, which in turn was connected to the shock tube and pumping apparatus. (Grease seals in the vacuum system were of inorganic material.) A mixture of PbEt_4 and neon was prepared by holding the temperature of the former at some point below room temperature and allowing the vapor to flow into the large flask. Calculation showed that 5 h were more than enough time for the vapor to achieve the saturated vapor pressure. Neon was then added to make a mixture of the desired concentration, since the saturated vapor pressure of PbEt_4 is well known.⁹ After allowing several hours for thorough mixing, the mixture was ready for introduction into the expansion chamber of the shock tube. A number of spectroscopic observations were made with shock heated PbEt_4 /neon mixtures and line intensities of Pb I lines measured and used to compute oscillator strengths: the results were one or two orders of magnitude below any previous measured values. A review of the procedure indicated our estimate of PbEt_4 concentration could have been erroneous. To verify this conclusion, the spectroscopic device for determination of electron density by H_{β} broadening was designed and built. Observations with this instrument confirmed that the electron concentrations in the shocked gas were an order of magnitude below those predicted on the assumption that the concentration of PbEt_4 remained unchanged after preparation of the mixture. To pin down the elusive PbEt_4 concentration, samples of the PbEt_4 /neon mixture

⁷ A. C. Kolb, H. Griem, and K. Y. Shen, *Astrophys. J.* **135**, 272 (1962).

⁸ W. A. Brown, Ph.D. thesis, University of Michigan (1964).

⁹ T. E. Jordan, *Vapor Pressure of Organic Compounds* (Interscience Publishers, Inc., New York, 1954).

were withdrawn from the shock tube just before firing the tube. Vacuum flasks containing the samples of mixture, as well as a control flask containing only neon, were analyzed for lead content both in vapor phase and on the walls of the flasks.¹⁰ The results were as follows: after 5 h, a mixture thought to contain 0.3% PbEt₄ contained only 0.07%, and at 2.2, 5, and 6 days contained concentrations of 0.058, 0.026, and 0.023%. The explanation for this deficiency was not found, but the measured concentrations were employed in all shock calculations. The chemical-colorimetric lead determinations were sensitive to about 0.5 micrograms of lead out of a total of about 2 μg in a sample flask. This uncertainty dominated all others in our experiments, and numerical calculations were made to determine the effects of variation of PbEt₄ concentration on emission line intensity, for the experiments reported here. We found that the fractional error in intensity was about 1.25 times the fractional error in PbEt₄ concentration, so that our reported *f*-values are uncertain to about 30%.

We now summarize the results of our Pb I oscillator strength determinations and compare them with those of other investigators. Table II, column 2, gives our mean values of the absorption *f*-values. (We measured, in fact, the *gf*-value, and employed the tables of Moore¹¹ to obtain degeneracies for the atomic energy states between which the transitions occur.) While the error associated with the absolute *f*-values is about 30%, the relative values are probably reliable to within 10%. The measurements of

¹⁰ Analysis of the gas samples was conducted by the Shuman Laboratory, Battleground, Indiana, and involved solution of the PbEt₄ in chloroform, followed by conversion to Pb ion and colorimetric comparison with solutions of known lead concentration in dithizone reagent. Any lead compound adhering to the walls from the sample flasks was removed and added to that collected from the vapor phase.

¹¹ C. E. Moore, National Bureau of Standards Circular 467 (1957), Vol. III.

TABLE II. Absolute oscillator strengths: Pb I.

| 1 wavelength, Å | 2 Present Work | 3 Penkin | 4 Helliwell |
|--------------------|----------------------|-------------|----------------|
| 3639.5 | 0.039 | 0.063 | 0.089 |
| 3683.5 | 0.070 | 0.116 | 0.17 |
| 4057.8 | 0.139 | 0.153 | 0.365 |

Penkin and Slavenas,¹² given in column 3, were made by the method of anomalous dispersion which has proved very successful for those lines accessible to the technique. Column 4 gives the results of Helliwell's¹³ theoretical calculation.

Spectral lines of Pb II were observed in emission from the shock heated gas. It was not possible to make definitive oscillator strength measurements on these lines, and our results are reported here only because no others are known to exist. For the line Pb II 4386.4 (²F_{5/2}⁰ → ²D_{3/2}), we find *gf* > 15; for the unresolved pair 4242.5 (²F_{5/2}⁰ → ²D_{5/2}) and 4245.1 (²F_{7/2}⁰ → ²D_{5/2}), we find *gf* > 15. Although the Coulomb approximation of Bates and Damgaard¹⁴ was not expected to apply to the Pb II lines discussed here, it was nevertheless tried and yielded *gf*-values of about one third those observed experimentally.

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¹² N. P. Penkin and I. Yu. Yu. Slavenas, Opt. i Spektroskopiya 15, 154 (1963) [English transl.: Opt. Spectry. (USSR) 15, 83 (1963)].

¹³ T. M. Helliwell, Astrophys. J. 133, 566 (1961).

¹⁴ D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. (London) A242, 101 (1949).