

ON THE $6s6p^2 \ ^3S_1$ LEVEL AND
THE CONFIGURATION-MIXING OF
THE $6s6p^2 \ ^4P_3$ LEVEL IN Tl I

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ABSTRACT

Experiments on the absorption spectrum of shock-heated Tl vapour have revealed a new Tl I doublet ($6^2P_{1/2,3/2}^o - 6s6p^2$ $^2S_{1/2}$). The profile of the Tl I ($6^2P_{1/2}^o - 6s6p^2$ $^4P_{3/2}$) autoionization feature has been obtained by experiments with a furnace and scanning monochromator, and the result is compared with the theory of "Beutler-Fano" resonances.

Identifications of the level-positions of the terms (4P , 2D , 2P , 2S), due to the sp^3 -configuration of Tl I, and our understanding of the combinations of these levels with those of the series spectrum have been less secure than in the cases of the analogous spectra Al I, through In I. An important contribution on the Tl I spectrum was made by Beutler and Demeter (1934) who studied the absorption spectrum of thallium vapour - produced with an absorption tube heated in a furnace - in the quartz-ultraviolet and Schumann regions, at a dispersion of $17\text{\AA}/\text{mm}$. They were able to identify transitions from the ground-level $6^2P_{1/2}^0$ to four levels - namely, $^4P_{1/2,3/2}$, $^2D_{3/2}$, $^2P_{1/2}$ - of the possible eight of sp^3 . The ground-term interval ($6^2P_{3/2}^0 - 6^2P_{1/2}^0$) being nearly 7800 cm^{-1} , the upper level $6^2P_{3/2}^0$ was negligibly populated at the low furnace temperatures used, so that the $J = 5/2$ levels of sp^3 were not accessible. Also, Beutler and Demeter did not report discovery of $6s6p^3\ ^2S_{1/2}$ and, in fact, presented an argument, based on intensity expectations associated with approach to jj-coupling, predicting absence of the line $6^2P_{1/2}^0 - 6s6p^3\ ^2S_{1/2}$. The argument is, however, suspect since

similar reasoning led to the false identification of the In I 1757Å line (Garton, 1954). The argument in the latter case has since been proved fallacious (Marr and Heppinstall, 1966a; Garton, Parkinson and Reeves, 1966).

Other relevant work on this portion of the Tl I spectrum was reported by Clearman (1952), who examined the lines emitted by a thallium arc in a nitrogen atmosphere. Clearman obtained the four lines of Beutler and Demeter and added three new combinations of the ground doublet, one of these at $\lambda_{\text{vac.}}$ 1685.4Å confirming the $sp^2 \ ^2P_{1/2}$ level, one at $\lambda_{\text{vac.}}$ 1847Å confirming $sp^2 \ ^2D_{3/2}$, and a line at λ_{air} 2209.7Å being interpreted as $6 \ ^2P_{3/2}^0 - 6s6p^2 \ ^4P_{5/2}$.

We have recently obtained absorption spectra of thallium vapour by means of the shock tube method. The temperature of the (argon-thallium) plasma being 5000 to 7000° K, the $6 \ ^2P_{3/2}^0$ level was populated sufficiently for absorption lines starting on it to be recorded. Consequently, we have found the line $6 \ ^2P_{3/2}^0 - 6s6p^2 \ ^2S_{1/2}$, and also its companion $6 \ ^2P_{1/2}^0 - 6s6p^2 \ ^2S_{1/2}$, which has proved to be reasonably strong, in contradiction to the expectation of Beutler and Demeter. The latter workers failed to observe the $^2P_{1/2}^0$ combination because they used the many-line spectrum of the H₂ molecule

as a background; the $H\alpha$ spectrum is poor in lines in the region concerned.

The line found by Beutler and Demeter at about 2007\AA , and ascribed to $6\ ^2P_{1/2}^0 - 6s6p^2\ ^4P_{3/2}$, has the asymmetrical type of profile recently explained by the work of Fano and collaborators (Fano, 1961; Fano and Cooper, 1965), and now described as a "Beutler-Fano resonance". These workers have shown that, if an autoionizing level has only one available continuum for the radiationless transition, then, on one side of the absorption maximum, there should be a minimum of zero-absorption cross section, a prediction that found its first verification in the work of Madden and Codling (1965) on the He I resonance $1s^2\ ^1S_0 - 2s2p\ ^1P_1^0$ near 200\AA . Since achievement of sufficient wave-number dispersion for adequate resolution of a line profile at such short wavelength is difficult, we have thought it worthwhile to examine the profile of the Tl I 2007\AA line because here again the autoionizing level, $6s6p^2\ ^4P_{3/2}$, has available only a single continuum - in this case, of even parity and $J = 3/2$, viz., $6s^2E(d)\ ^3D_{3/2}$. The line profile proved wide enough for full resolution at the dispersion ($8.3\text{\AA}/\text{mm}$) of a McPherson one-meter scanning vacuum-spectrometer. A

furnace was used to provide a column of thallium vapour 50 cm long, at about 850° K, a hydrogen positive-column discharge provided a background continuum, and an EMI 6256 quartz-window photomultiplier served as detector.

The plate shows a set of spectra obtained with the shock tube apparatus for varying densities of Tl vapour. The four lines discovered by Beutler and Demeter are present, and a new doublet with components at 1302Å and 1449Å, exhibiting large autoionization broadening, can be seen. So far as the LS-designation is meaningful, the upper level here concerned will be $6s6p^2 \ ^2S_{1/2}$, which is therefore placed 76804 cm^{-1} above $6 \ ^2P_{1/2}$. The shock pictures also contain Clearman's line at 1685Å, viz., $6 \ ^2P_{3/2}^0 - 6s6p^2 \ ^2P_{1/2}$. We have been unable to confirm his line $6 \ ^2P_{3/2}^0 - sp^2 \ ^2D_{3/2}$ at 1847Å; this would show as an extremely diffuse absorption feature, and its absence is not surprising, from the intensity rules for a $^2P^0 - ^2D$ multiplet. Our plates show an extremely weak diffuse absorption line at about the position $\lambda_{\text{vac.}} = 2210.4\text{Å}$ given by Clearman for $6 \ ^2P_{3/2}^0 - 6s6p^2 \ ^4P_{5/2}$. A considerably stronger line present on our exposures, at $\lambda_{\text{vac.}} = 2231.5\text{Å}$, seems definitely ascribable to Tl I. The possibility exists that this is the $^4P_{5/2}$ combination, though it

could equally well be the forbidden transition $6^2P_{1/2}^0 - 6^2F^0$, since several members of $6^2P_{3/2}^0 - n^2F_{5/2}^0$ ($n = 5, 6, 7$) are present in absorption at high vapour densities.

The line $\lambda_{\text{air}} 2671.0$ mentioned by Beutler and Demeter (1934) as being reported by former workers, is present, weak and quite sharp, on our spectra. It can be safely ascribed to $6^2P_{3/2}^0 - 6s6p^3\ ^4P_{1/2}$, and the measurements reported recently by Reeves, Garton and Bass (1965) on its companion $6^2P_{1/2}^0 - 6s6p^3\ ^4P_{1/2}$ (a close doublet unresolved in the present work) indicate the improved wavelength $\lambda_{\text{air}} = 2671.84$.

The profile of the "resonance" feature near 2007\AA , now interpreted as a transition from $6^2P_{1/2}^0$ to the mixture of states $6s6p^3\ ^4P_{3/2}$ and $6s^2E(d)\ ^2D_{3/2}$, is shown reduced to absorption cross section by the full line in Fig. I. The profile was obtained, as mentioned above, with a furnace and with the scanning monochromator resolving 0.15\AA . The scale of absolute cross section has been taken from the recent revision by Marr and Heppinstall (1966b) of Marr's (1954) measurements of the $\lambda 2007$ profile, made with a fluorite prism spectrograph and photographic photometry.

Fano (1961) and collaborators (Fano and Cooper, 1965) have shown that for autoionization into a single continuum,

the absorption cross-section profile should follow the formula

$$(1) \quad K(\nu) = \text{const.} \frac{(q + \epsilon)^2}{1 + \epsilon^2},$$

where q is a "line profile index" and $\epsilon = \frac{2(\nu - \nu_0)}{\Gamma}$ is a dimensionless "reduced" energy variable, which denotes the distance of the point at frequency ν in the profile from the idealized "resonance" frequency ν_0 corresponding to the auto-ionizing state when expressed as a multiple of the resonance half-width $\Gamma/2$.

The absorption cross section (1) takes a maximum $(1 + q^2)$ at $\epsilon = 1/q$, and a zero minimum at $\epsilon = -q$. Consequently, q can be obtained from the height of the maximum in Fig. I, relative to the level of the unperturbed continuum absorption, and Γ can then be found from the distance $\epsilon_{\text{max}} - \epsilon_{\text{min}} = q + 1/q$ along the horizontal axis.

From the full curve of Fig. I we thus find $q = 2.30$, $\Gamma = 1.36 \times 10^{13} \text{ sec}^{-1}$. Points corresponding to the experimental data of Marr (1954) are marked and, while these generally conform, it is clear that the instrumentation available to him did not permit full resolution of the maximum of the line profile. With the values of q and Γ derived as

above, we have shown in Fig. I the course of equation (1), normalized to the experimental data at the position of the maximum. The agreement between theory and experiment is excellent, save for the departure at the short-wavelength side, which can be reasonably ascribed to departure from the assumption contained in (1) that the absorption cross section of the unperturbed continuum does not change appreciably over the width of the resonance.

The portion of the work reported here, performed with the shock tube apparatus, has added one important new level of Tl I and provided definite confirmation of another previously identified by the work of Beutler and Clearman. The work with the furnace has provided the best quantitative check of a Beutler-Fano resonance to date. However, several features of this absorption spectrum still require understanding. The $sp^2 \ ^4P_{5/2}$ level cannot be said to have been determined with any certainty. The $^3D_{3/2}$ level, which could be expected to give a strong combination with the upper level of the ground-term, has not been revealed. Likewise, the $sp^2 \ ^2P_{3/2}$ level has not been found. Probably the use of the LS-symbols has little significance in this configuration of Tl I, and fairly extensive calculation will be necessary to account for peculiarities outstanding.

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Tl I $6s^2 6p^2 P_1^0 - 6s 6p^2 \text{ } ^4P_{3/2}$

BEUTLER - FANO RESONANCE $\lambda 2005 \text{ \AA}$

$q = 2.30$

$\Gamma = 1.36 \times 10^{12} \text{ sec}^{-1}$

..... THEORETICAL FANO PROFILE

□ MARR'S EXPERIMENTAL POINTS

— PRESENT WORK

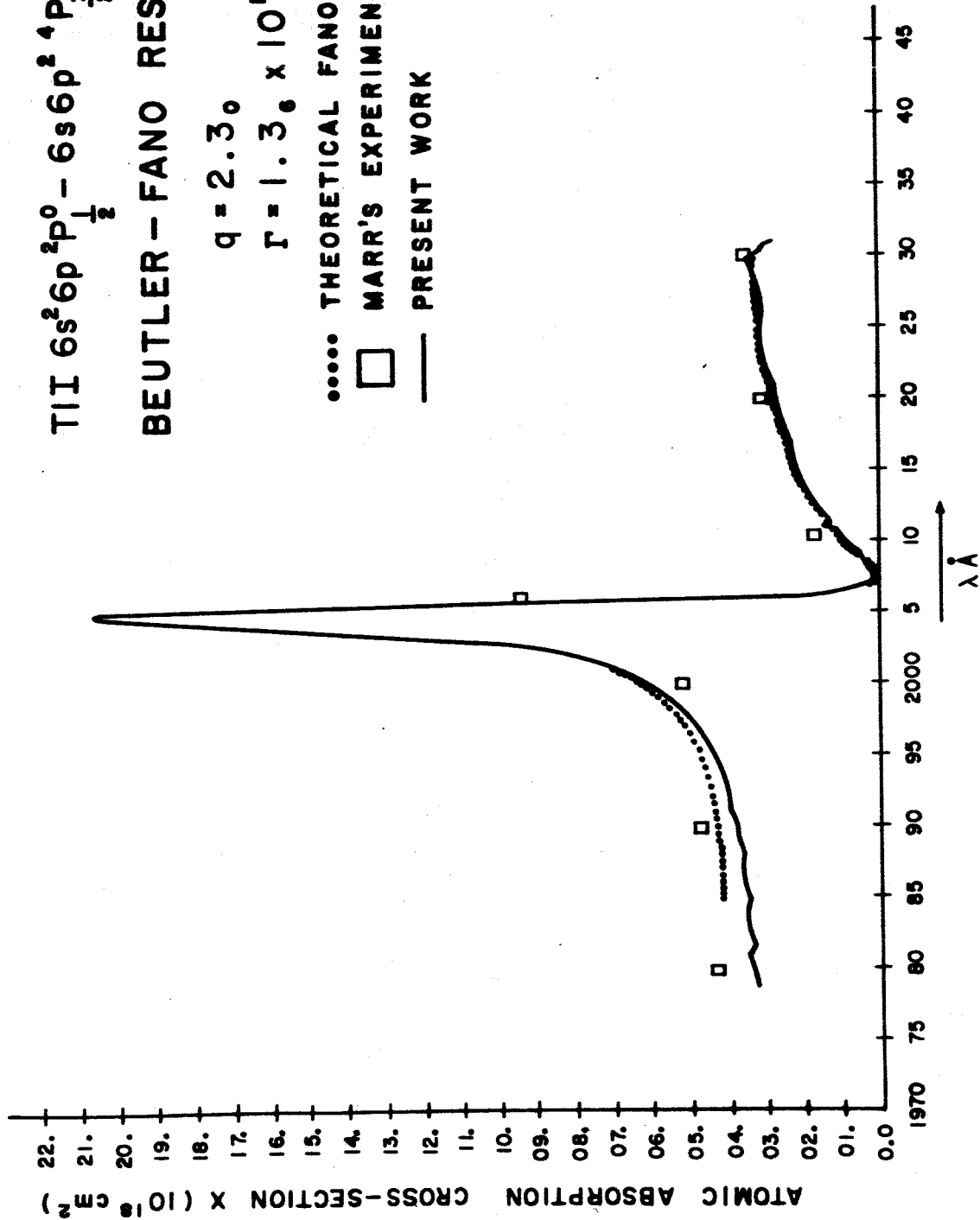
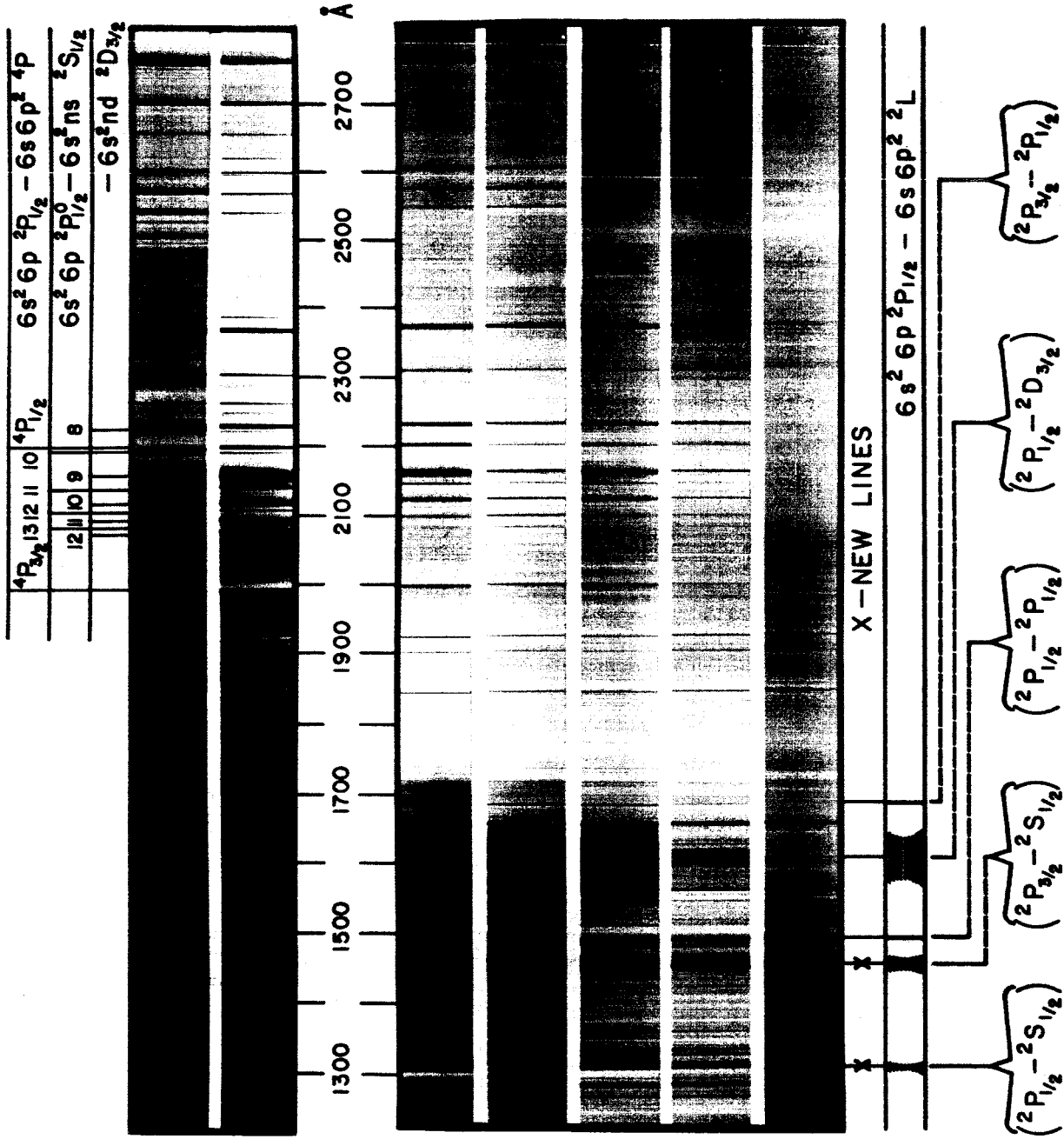


Figure I. The Tl I Resonance $6s^2 \text{ } ^4P_{3/2}^0 - 6s 6p^2 \text{ } ^4P_{3/2}$.



ABSORPTION SPECTRUM OF SHOCK-HEATED THALLIUM

Plate I. Absorption Spectrum of Shock-Heated Thallium.

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