Granneman (*J. Phys.* **B8,** 1617; 1975). Much to everyone's surprise large discrepancies, of up to four orders of magnitude, were found between experiment and until then currently accepted theory. A predicted deep minimum of 2.6 eV photon energy in the two-photon ionisation curve arising from cancellation of 6p and 7p intermediate state contributions is entirely absent in the experimental data. Three years later, after much theoretical and experimental work, the problem remains, with no sign of a successful explanation. Similar paradoxical situations exist in the multiphoton ionisation of other atoms.

The experimental two-photon ionisation rates, P_2, are measured away from intermediate atomic resonances and at low enough laser intensities I to avoid saturation. Then the two-photon ionisation generalised crosssection σ_2 at laser frequency ω can be defined through $P_2 = \sigma_2 \langle I^2 \rangle$ and σ_2 is described by the second order perturbation result

$$\sigma_2 \propto \left[\sum_n \frac{\langle f | r | n \rangle \langle n | r | g \rangle}{\omega_n - \omega} \right]^2$$

The atom is presumed to start in some initial state $|g\rangle$, end up in a continum state $|f\rangle$ and we need to sum all intermediate states $|n\rangle$ of energy $\hbar\omega_n$. Often, as here in Cs at 2.6 eV, there is destructive interference amongst the terms in the sum: all signs are equal except energy denominators and σ_2 should exhibit a deep minimum sometimes called a Fano or Cooper minimum. Problems facing the theorist involve finding accurate (although necessarily approximate) values for atomic wavefunctions using quantum defect, model potential or other methods and then to perform the summations. The existence and properties of the minimum have been reinvestigated by Teague *et al.* (*Phys. Rev.* **A14,** 1057; 1976) again assuming the validity of second order perturbation theory. They find the position of the minimum is insensitive to the choice of wavefunctions. There is some disagreement between theoretical results obtained by different methods, but they all differ very much more from experiment than from each other.

The original experiments of Van der Wiel *et al.* were performed using the nine argon-ion laser wavelengths available, and were calibrated by normalisation to a known one-photon cross section measured using frequency doubled laser light. The quadratic intensity dependence of P_2 (and therefore the absence of saturation) was checked using neutral density filters. Since it is only a two-photon process, photon statistics of the laser light are relatively unimportant (they can contribute a factor of two at most). One problem is the contribution dimers make to the ion signal by processes such as

$$Cs_2 + 2\hbar\omega \rightarrow Cs_2^+ + e$$

and

$$Cs_2 + 2\hbar\omega \rightarrow Cs^+ + Cs^- \text{ h } Cs^+ + Cs + e$$

Relatively few dimers can provide a larger count rate than the numerically superior free atoms because they are resonantly enhanced and have a large density of resonant states. This molecular effect potentially can fill in the experimental minimum, but Van der Wiel and colleagues at FOM have studied these processes in detail (Granneman *et al.* *J. Phys.* **B9,** 865; 1976; Klewer *et al.* *J. Phys.* **B10,** 2809; 1977) and believe they have the dimers under control and that the discrepancy is not due to molecular background. Another possibility was that the mimimum lies below the lowest energy available from an argon ion laser. This possibility seems now to have been eliminated (Klewer *et al. J. Phys.* **B10,** L243; 1977) by using an argon-ion pumped Rhodamine 6G dye laser to study two-photon ionisation at photon energies from 2.2 eV to near the two-photon threshold at 1.95 eV. Provided the temperature is raised sufficiently to remove dimers no detectable atomic two-photon ionisation remained in the wavelength at the (lower) intensities available from their dye laser. The data from all the wavelengths is compared with the best current theory in Fig. 1. In the same paper the ratio of the ion count rates obtained from two-photon ionisation of Cs atoms using linearly and circularly polarised light at the nine argon-ion wavelengths were measured. Again there is disagreement with theory, with the experimental ratio (σ_2(circ)/σ_2(lin)) lying significantly below the 'best' values of Teague *et al.* except close to a $7P_{1/2}$ intermediate resonance.

So we are left with a considerable problem. The approximate position of the Cooper minimum in the two-photon ionisation is determined by only a few matrix elements corresponding to transitions to nearby levels. Other levels shift the minimum by only a small amount.

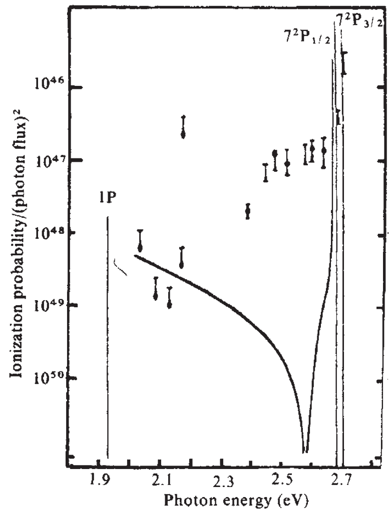

Fig. 1 Two-photon ionisation probability of Cs as a function of photon energy. **I**, Granneman and Van der Wiel (*J. Phys.* **B8,** 1617; 1975); ● Klewer *et al.* (*J. Phys.* **B10,** L243; 1977), ⊥ upper limit found in the same ref.; full curve, Teague *et al.* (*Phys. Rev.* **A14,** 1057; 1976) theory. (Taken from Klewer *et al.*)

It would require a change in sign of either the matrix elements $\langle 6p|r|6s \rangle$ or $\langle 7p|r|6s \rangle$ for the deep minimum not to occur. Obviously more theoretical work on the calculation of σ_2 is needed. Even the validity of second-order perturbation theory to describe the two-photon ionisation has been investigated, by Crance and Feneuille (*Phys. Rev.* **A**, in the press) who studied the time development of the pulsed photoionisation using a model introduced by Armstrong, Beers and Feneuille (*Phys. Rev.* **A12,** 1903; 1975). They have found some effects due to the finite pulse length, but their model is a little idealised. More experimental work is needed and this is being undertaken in various laboratories. Looking for a minimum is hard when background molecules are only too eager to fill the sought-for trough and future experiments will need to pay special attention to this problem. □

NATURE

A hundred years ago

Dr. Vohl, of Cologne, has adopted an ingenious method of determining the impurities in the Rhine, which consists in analysing the boiler incrustations of the river steamers, as well as the concentrated residues remaining in the boilers after passing over a certain distance. By this means he has detected the presence of a large amount of arsenious acid in the river water—resulting chiefly from the aniline and dyeing establishments—as well as other poisonous substances. An unusually high percentage of phosphoric acid showed that the sea was daily absorbing vast quantities of the most valuable fertilising material from the soil of Germany.

Another sitting of the enlarged Council of the Observatory of Paris was held on December 9. The councillors passed a resolution for an increase of the salary of the astronomers and auxiliary astronomers, the maximum pay of the former to be 10,000 francs instead of 8,000, and of the second 7,000 instead of 6,000. They propose to the Government to place the appointment of the director of the establishment partly in the hands of the Academy of Sciences and partly in the hands of the Council, the Minister to have only the privilege to choose between both presentations.

From *Nature* **17,** 13 December, 131; 1877.