Absorption Spectra of Excited Atoms and Excited Ions produced by Isothermal Flash Photolysis of Metal Carbonyls in the Gas Phase

SPIN-ORBIT multiplets of atoms in ground electronic states are particularly interesting for the investigation of electronic energy transfer; simple theoretical considerations indicate that the relaxation rates correlate with the magnitude of the internal energy changes[1]. Measurements of the formation and decay of excited selenium (4^3P) and iodine (5^2P) have already been reported[2,3]. We have recently shown that the flash photolysis of iron pentacarbonyl ($Fe(CO)_5$), which has been investigated in some detail, and of nickel carbonyl ($Ni(CO)_4$), can be used to produce excited atoms in gases under isothermal conditions. Spin-orbit relaxation rates can be measured by kinetic spectroscopy, before polymerization of the normal atoms occurs. The method is general to volatile transition-metal compounds, and the observations therefore reveal numerous experimental systems for energy transfer studies.

A flash-photolysis apparatus of standard design produced a 1700-J light pulse in 5×10^{-5} sec, and absorption spectra were recorded with a Hilger Medium Quartz Spectrograph. In experiments with $Fe(CO)_5$ at pressures of 0·005–0·001 mm of mercury, and argon added to a total of 10–50 mm of mercury, the disappearance of the far ultra-violet continuum of the carbonyl was complete in the first 3×10^{-5} sec of the flash. The absence of any significant rise in temperature may be shown by calculation, assuming each $Fe(CO)_5$ molecule to absorb five light quanta at 2000 Å, or else demonstrated experimentally by deducing the equilibrium concentration in the a^5D_4 and a^5D_3 states from the observed line intensities in absorption and the published oscillator strengths[4].

Table 1 shows the states of atomic iron detected in absorption in flashed $Fe(CO)_5$/argon mixtures. The energies correspond to the lowest of the spin-orbit multiplets[5].

The highly excited levels rapidly decay to populate the spin-orbit components of the a^5D state; relaxation of the a^5D multiplets occurs in 10^{-4} sec. The calculated temperature rise, the rapid decay of the excited atoms, and the increased rate of decay caused by addition of traces of polyatomic gases prove that the extent of electronic excitation is greatly in excess of a Boltzmann distribution at the translational temperature, which remains close to 300° K. (With partial pressures of $Fe(CO)_5$ of the order of 0·1 mm of mercury, relaxation is extremely fast and the population in the lower electronic states is due to a substantial temperature rise.) Provided the $Fe(CO)_5$ is completely destroyed by the flash, the populations in the a^5D states are independent of the energy of the flash, and the most highly excited distributions occur at the shortest delay times. Photodissociation evidently produces atomic iron in a range of electronic states, for example:

$$\text{Fe CO} + h\nu \rightarrow \text{Fe}^* + \text{CO}$$

Our original objective was to measure the rate of the $a^5D_3 \rightarrow a^5D_4$ (416 cm^{-1}) transition in argon, and the probability of deactivation has been recorded as $0·2 \times 10^{-4}$ at 300° K. This is significantly slower than vibrational relaxation of non-hydrides, if the same energy is transferred to translation.

Flash photolysis of $Fe(CO)_5$ provides the first example of the production of ions in a gas at concentrations ($\sim 10^{12}$ ions/c.c.) suitable for measurement by kinetic absorption spectroscopy. Fig. 1 shows the formation and decay of Fe^+ (a^6D). The relative populations of the five multiplets

Table 1

State	Energy (cm^{-1})	State	Energy (cm^{-1})
a^5D	0	a^3H	19,360
a^5F	6,928	b^3F	20,641
a^3F	11,976	a^3G	21,715
a^5P	17,550	z^7F	22,650
a^3P	18,378	b^3P	22,838
z^7D	19,350	z^7P	23,711

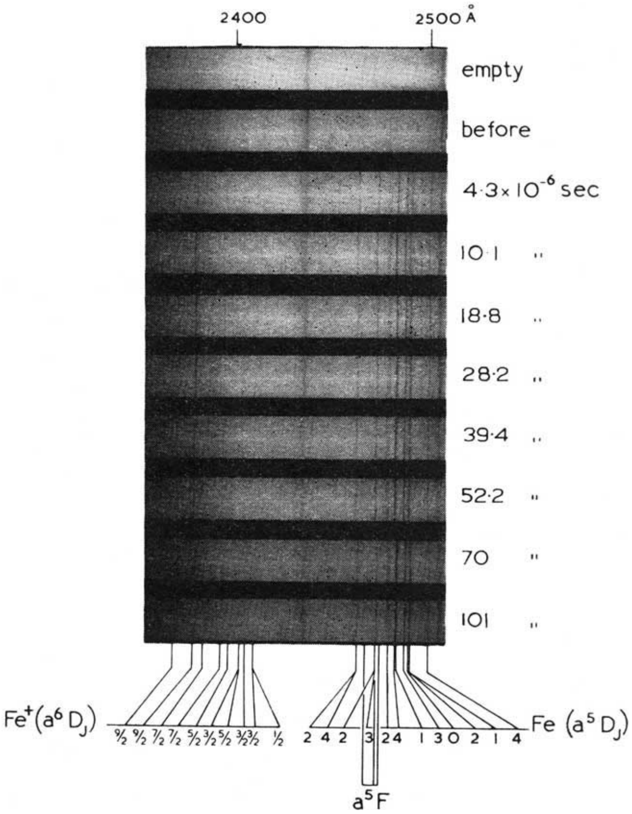

Fig. 1. Formation and decay of $Fe^+(a^6D)$ in flashed $Fe(CO)_5$ vapour

vary during and following the flash. We have also shown that the total concentration of ions increases linearly with flash energy. Ultra-violet radiation at the 1850 Å oxygen cut-off is 10,000 cm^{-1} short of the 7·40 eV ionization potential of atomic iron in the a^5D_4 state. However, all states above a^5F suffer ionization by secondary light absorption. The decay rate of the ions increases with increasing pressure, which may suggest that removal is by three body processes.

We have made preliminary measurements of the non-Boltzmann electronic-distribution of atomic nickel, produced by flash photolysis of $Ni(CO)_4$.

A. B. CALLEAR
R. J. OLDMAN

Physical Chemistry Laboratory,
University of Cambridge.

[1] Callear, A. B., *App. Optics, Second Laser Suppl.*, 145 (1965).
[2] Callear, A. B., and Tyerman, W. J. R., *Trans. Faraday Soc.*, **61**, 2395 (1965).
[3] Donovan, R. J., and Husain, D., *Nature*, **206**, 171 (1965).
[4] Corliss, C. H., and Bozman, W. R., *Transition Probabilities*, Nat. Bur. Stand. Monograph 53 (1962).
[5] Moore, C. E., *Atomic Energy Levels*, Nat. Bur. Stand. Circular 467, **2** (1952).

Dynamic Fatigue in Glasses

THE static fatigue of glasses is a well-known and well-documented phenomenon (see, for example, ref. 1), but the only investigation of cyclic loading fatigue known to the authors is that of Gurney and Pearson[2], who reported a negative result. Perhaps in view of this result and of the near ideal brittle behaviour of glasses the investigation of cyclic loading fatigue appears to have been neglected. Recent results obtained in these laboratories as part of an extensive investigation of the strength of fused silica have indicated that a real cyclic fatigue effect may exist in this material. Circumstances have prevented a full investigation and confirmation of the effect, but in view of the importance of the problem the preliminary results would seem worth reporting here.

In the upper part of Fig. 1 a comparison is made between the static fatigue life under constant tensile

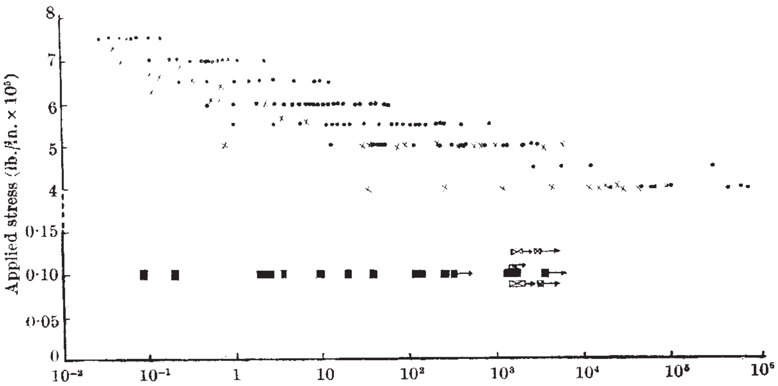

Fig. 1. Static and dynamic fatigue of silica. ●, Static fatigue of silica fibres in tension; ×, dynamic fatigue of silica fibres in tension; ⊠, static fatigue of silica rods in bending; ■, dynamic fatigue of silica rods in rotating bending. ■→ and ⊠→ indicate samples surviving life shown

stress, and the fatigue life under cyclic tensile stress, of virgin silica fibres[3]. The repetition rate of cyclic loading was in the range 30–75/min and the stress varied from zero to the nominal stress plotted on the graph. Loading was achieved by picking up and releasing a dead weight with a cam and the pulse shape was a flat-topped half sine curve so that stress was only applied to the fibre for less than one half the plotted times. Particularly significant are the early failures at 400,000 lb./in.^{2}.

In the lower part of Fig. 1 a comparison is made between static fatigue in cantilever loading, and rotating bending fatigue in cantilever loading, of mechanically damaged 1 mm diameter fused silica rods at much lower strength-levels. The cycling rate here was very much higher (3,700/min) and the cycle approximated to a full sine curve with the stress reversing from the maximum tensile value shown in Fig. 1, through zero, to the same value in compression. At the same stress and over the same time scale, no failures were observed with the comparable static bending fatigue specimens.

I. WHITNEY
J. W. JOHNSON
B. A. PROCTOR

Rolls-Royce Ltd.,
Old Hall, Littleover, Derby.

[1] Mould, R. E., and Southwick, R. D., *J. Amer. Ceram. Soc.*, **42**, 542, 582 (1959); **43**, 160 (1960); **44**, 481 (1961).
[2] Gurney, C., and Pearson, S., *Glass and Ceramics*, **10**, 115 (H.M.S.O., 1952).
[3] Morley, J. G., Andrews, P. A., and Whitney, I., *Phys. Chem. Glass.*, **5**, 1 (1964).

BIOCHEMISTRY

Acetylcholine-like Activity of Acetyl-l-carnityl CoA in the Brains of Narcotized Rats

NUMEROUS investigators[1–5] have shown that the administration of narcotic drugs to animals causes an increase in the brain acetylcholine-like activity. Most of these authors[1–4] believed that the material extractable from such brains was acetylcholine and this was based largely on the results obtained from experiments performed with the parallel bio-assay technique. Hosein and Koh[6] and Hosein, Rambaut, Chabrol and Orzeck[7] have shown that the method of parallel bio-assay is incapable of identifying acetylcholine in mixtures of substances which possess acetylcholine-like activity. In addition, these latter authors showed that the various test preparations used in the method of parallel bio-assay could not discriminate between mixtures of substances which possessed acetylcholine-like activity, even when non-natural substances were used.

Hosein and his associates[8,9] have shown by microchemical analysis that, of the material with acetylcholine-like activity extractable with trichloroacetic acid from brain, 20 per cent of this activity was due to a mixture of choline esters and the remainder to a mixture of butyrobetaine Co*A* esters. Numerous investigators[10–13] have since performed chromatographic separation of similar brain extracts and, although the peak of acetylcholine-like activity on the chromatogram differed in each such attempt (range from R_F 0·05 to 0·9), in every instance it was concluded that the active material was due solely to acetylcholine. Recently, Maslova[14], in contradicting the findings of Birks and MacIntosh[15] while confirming those of Hosein and Proulx[16], has shown that chemically identifiable acetylcholine in trichloroacetic acid extracts of the superior cervical ganglia accounted for only one-fifth of the amount of such material determined by bio-assay.

Hosein and Ara[5] suggested, on the basis of chromatographic analysis of trichloroacetic acid extracts of narcotized rat brain, that the material with acetylcholine-like activity was probably a butyrobetaine Co*A* ester rather than a choline ester. Hosein and Koh[17] showed on the basis of chromatographic and chemical analyses that the material with acetylcholine-like activity extractable from narcotized brain was acetyl-1-carnityl Co*A*. The experiments described here represent an extension of this work.

Sixty rats were deeply narcotized with pentobarbital (65 mg/kg) for 30 min. After that time the animals were killed and the brains were homogenized (fifteen at a time) in 5 per cent trichloroacetic acid. This extract was prepared for bio-assay with the frog rectus preparation as previously described[5,8]. The total activity found in the sample was equivalent to 276 μg acetylcholine chloride which was then divided into two equal parts, *A* and *B*. A solution containing 138 μg of crystalline acetylcholine chloride was added to sample *B*. The two samples *A* and *B* were evaporated to dryness and then converted to their tetrachloroaurate derivatives[8]. In each sample there was material which formed an immediate precipitate with the auric chloride and which could easily be collected by centrifuging as crystals fraction (i). When the supernatant fluid of each sample was left in the refrigerator for a further period of 4–5 days, crystals fraction (ii) was collected. The substances in the various fractions were identified by melting-point determination.

The results obtained from such analyses are shown in Table 1. It can be seen that the added acetylcholine was readily recovered and identified in crystals fraction (i) of sample *B*. No such material could be found in the corresponding fraction of sample *A*. Crystals fraction (ii) of both samples *A* and *B* contained material that melted at 120°–124° C which, in other work, we have shown to be acetyl-1-carnitine[9]. It was observed in previous work that preparation of the tetrachloroaurate derivatives of the Co*A* ester of the butyrobetaines in tissue extracts destroys the thiol ester linkage. It was assumed that a similar reaction took place in this extract.

In these experiments a small amount of materials in crystals fraction (i) only was found to have a melting-point of 130° C. Hosein and Proulx (unpublished) have found that the tetrachloroaurate of γ-butyrobetainyl choline also melts at 130° C. Further chemical analyses are, however, required to identify these particular crystals.

Table 1. MELTING POINT DETERMINATIONS OF TETRACHLOROAURATE DERIVATIVES PRESENT IN TRICHLOROACETIC ACID EXTRACTS OF NARCOTIZED RAT BRAINS

Sample	Melting point (° C) of crystal fractions (i)	(ii)	Probable substance
A	—	120–124	Acetyl-1-carnitine
	130	—	(γ-Butyrobetainyl choline)?
B	—	120–124	Acetyl-1-carnitine
	130	—	(γ-Butyrobetainyl choline)?
	165–167	—	Acetylcholine