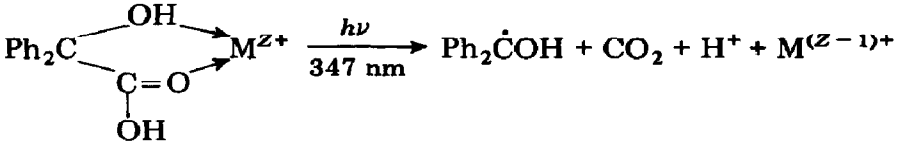
Letter to the Editor

Comments on "Oscillatory reactions observed in flash photolysis — an artefact?"

We attributed [1] our observation of damped oscillations of the optical transient in the system



($M^{Z+} \equiv Fe^{3+}$, Ag^{+}, Cu^{2+}), on balance, to a chemical rather than a physical origin because (a) the oscillating feature shows a highly characteristic visible absorption spectrum extending to 950 nm which is of a highly reproducible character, (b) the use of UO_2^{2+} (which also absorbs strongly at 347 nm) as the sensitizing photo-oxidant failed to produce oscillations, yielding only the intense spectrum of $Ph_2\dot{C}OH$ (λ_{max} = 542 nm), and (c) the reduction in the laser pulse intensity by a factor of 10 failed to suppress the oscillations, only reducing their amplitude. Again, photoredox systems containing metal ions of variable oxidation state are exactly those which might be expected to be involved in such behaviour should it exist. However, Grummt's observation [2] of essentially identical kinetic behaviour in a quite unrelated chemical system (*o*-naphthoquinone diazide in methanol) together with his piezoelectric detection measurements must now move the balance of argument decisively in favour of a purely physical explanation of these two cases, despite the development of a highly relevant mathematical model by Micheau *et al.* [3]. This generates damped oscillations, even on the 10 μs time scale, of excited states in biphotonic photochemical systems. Indeed, Micheau *et al.* conclude with a warning that such time-dependent behaviour should be critically analysed before being rejected as artificial. However, in the two systems discussed here it must be concluded that we are dealing with a sound wave, although the origin of the spectrum remains to be clarified.

1 T. J. Kemp and L. J. A. Martins, *J. Chem. Soc., Chem. Commun.*, (1979) 227.
T. J. Kemp and L. J. A. Martins, in W. J. Gettins and E. Wyn-Jones (eds.), *Techniques and Applications of Fast Reactions in Solution*, Reidel, Dordrecht, 1979, p. 549.
2 U.-W. Grummt, *J. Photochem.*, *22* (1983) 289.
3 J.-C. Micheau, S. Boué and E. Vander Donckt, *J. Chem. Soc., Faraday Trans. II*, *78* (1982) 39.

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(Received January 31, 1983)

0047-2670/83/$3.00 © Elsevier Sequoia/Printed in The Netherlands