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Research Interests: structural chemistry, electron diffraction, computational chemistry, short-lived species



Chemistry never ceases to amaze, and we are always reading about new technologies and products – materials, medicines, chemicals with special properties. To make their work efficient, chemists need to be able to predict the properties of target molecules, and to understand the routes to these molecules, and the rates at which reactions will take place. Techniques for determining molecular structures are therefore of primary importance.

Nowadays computers can predict structures of many molecules accurately, and they may also model gas-phase reactions. However, the programs use standard information from experimental gaseous structures, so new, accurate information from gas-phase experiments is always required. There is a mass of gaseous structural information for stable molecules, but information about short-lived or unstable species is much harder to obtain. Data are scarce, although they are essential for modelling reaction pathways and thus predicting rates of reactions. My research is geared towards providing this information. Research areas include the structure determination of short-lived species using combined FVP-GED techniques, and the structure determination of stable radicals.

**Short-lived species** are generated using flash vacuum pyrolysis (FVP) techniques. The FVP and GED apparatus are coupled, and the unstable species are passed into the diffraction chamber where structural data is collected. Very-high temperatures are required for this work, as the short-lived species are usually generated at temperatures > 900 K.

**Generating stable radicals** from sterically loaded systems is in the very early stages of experimental investigation. The systems  $Z_2R_4$  /  $ZR_2$  [ $Z = P$  or  $As$ ,  $R = CH(SiMe_3)_2$ ] provided the first known examples of molecules with relatively normal strong Z-Z bonds, which required no additional energy to break. The driving force for dissociation is the conformational change, which allows relaxation of the steric strain upon dissociation. This led to the term 'jack-in-the-box' molecules being applied to these systems. Other systems have been predicted to behave in this manner, although no experimental work has been carried out on them. Work is currently underway to examine the process of dissociation in other symmetric and also asymmetric systems using experimental and theoretical methods.

### Selected recent publications

1. "Supersilyl radicals from the dissociation of superdisilane observed by gas electron diffraction." S. L. Masters (née Hinchley), D. A. Grassie, H. E. Robertson, M. Hölbling and K. Hassler, *Chem. Commun.*, 2007, 2618
2. "The molecular structure of tetra-*tert*-butyldiphosphine: an extremely distorted, sterically crowded molecule." S. L. Hinchley, H. E. Robertson, K. B. Borisenko, A. R. Turner, B. F. Johnston, D. W. H. Rankin, M. Ahmadian, J. N. Jones and A. H. Cowley, *Dalton Trans.*, 2004, 2469
3. "Dynamic interaction of theory and experiment: total determination of the gas-phase molecular structure of tri-*tert*-butylphosphine oxide ( $OPBu^t_3$ )." S. L. Hinchley, M. F. Haddow and D. W. H. Rankin, *Dalton Trans.*, 2004, 384.
4. "Conformational analysis with both experimental and computational data for both gaseous and crystalline phases: unexpected interactions in N-methylchloroacetamide." S. L. Hinchley, H. E. Robertson, L. J. McLachlan, C. A. Morrison, D. W. H. Rankin, S. J. Simpson and E. W. Thomas, *J. Phys. Chem. A*, 2004, **108**, 185.
5. "Spontaneous generation of stable pnictinyl radicals from "Jack-in-the-Box" dipnictines: a solid-state, gas-phase, and theoretical investigation of the origins of steric stabilization." S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. Voigt, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne, P. P. Power, *J. Am. Chem. Soc.*, 2001, **123**, 9045.