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CONCLUSIONS AND FUTURE DIRECTIONS*

In 1937, Davisson and Thomson received the Nobel Prize ‘for their experimental discoveries of the diffraction of electrons by crystals’. Earlier in the century, X-ray diffraction from crystals had been discovered; but, for gases, it was Debye and co-workers[1, 2] who showed that X-ray scattering patterns are rich with structural information, despite the randomness in the position and orientation of the gaseous molecular samples. Over the past 70 years, ever since the pioneering work of Mark and Wierl,[3] gas phase *continuous-beam* electron diffraction has become a powerful tool for studying

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* From Srinivasan, R.; Lobastov, V.A.; Ruan, C.-Y.; Zewail, A.H., *Helv. Chim. Acta*, **2003**, *86*, 1762.

the *static* nature of molecular structures. Within just five years of the first GED experiment, Brockway[4] listed in his review the structures of 44 inorganic and 103 organic molecules determined by GED. Since then, thousands of *static* molecular structures have been reported in the literature.[5] Aided by advances in instrumentation, theoretical insights, and computational analysis procedures, the field has witnessed several stages of evolution—the visual method, the sector-microphotometer method, and now, the ultrafast imaging of transient structures, as noted by Jerome Karle.[6] The central theme in ultrafast electron diffraction (UED) is the elucidation of the structural dynamics of *transient* molecular entities.

Reaching the spatiotemporal resolution on the atomic scale is the driving force behind the development of UED, the subject of this thesis. The current state-of-the-art in resolutions and sensitivity of UED (0.01 Å, 1 ps, and 1%, resp.), together with the theoretical advances made, make possible the freezing of transient structures, leading to studies of diverse molecular phenomena hitherto not accessible to other techniques. Of particular significance is the ability to observe evolution of structures on complex energy landscapes, including those far from equilibrium and with no heavy atoms.

This work has detailed the temporally and spatially resolved molecular structures, elucidated by UED, in diverse chemical phenomena. These include structures in radiationless transitions, structures in non-concerted organic reactions, structures in non-concerted organometallic reactions, structures of carbene intermediates, dynamic pseudorotary structures, non-equilibrium structures, and conformational dynamics on complex energy landscapes. Figure 10–1 shows the scope of UED applications that has been achieved in our laboratory at Caltech.

On the ultrashort timescale, both the rotational and vibrational motions of molecules are coherent; a degree of order is imposed on the otherwise isotropic sample at equilibrium. It is, therefore, necessary to consider the structural changes, both in this regime of coherent dynamics, and when coherence is subsequently lost. The current time resolution allows us to determine both the *structure* and the *population* of transient intermediates at each instant in time. It is also possible to exploit the coherent motion of atoms to observe new structural features as revealed by previous theoretical studies on the impact of rotational and vibrational coherences on the scattering pattern.[7] It has been shown that an additional dimension of imaging can be achieved at times when coherence is induced or recovered—in a sense, Debye's ring pattern begins to approach the diffraction from a crystalline sample. The X-ray crystallography method of using different crystal orientations to map out the structure of the unit-cell can be imitated in UED by exciting different orientations.[8]

The first three generations of UED have been devoted to studies of isolated, complex structures. Currently, in this laboratory, a major step forward in the evolution of UED is the development of the fourth-generation apparatus (UED-4)[9-11] designed for diffraction studies of surfaces and macromolecules on the ultrafast timescale, thus opening up the world of condensed phases and biology. With the electron-pulse sequencing of the diffraction-difference method, the six-orders-of-magnitude higher cross-section of electron scattering (compared to X-rays), and the development of femtosecond pulsed-electron sources,[12-14] the technique is poised to reach single molecule studies of complex structures.[15-17]

In December 1999, Philip Ball of *Nature* observed,[18] "Diffraction on the 'molecular' timescale of femtoseconds is an infant discipline which promises wonders once perfected, but which is capable right now of only the crudest of impressionistic sketches: blurred images of lattice dynamics, showing evidence of rapid change but without a single molecule (let alone an atom) in focus. The static photography of the Braggs has yet to produce its first movie." UED-3 has not only succeeded in bringing isolated molecules into sharp focus but has also captured the crucial 'freeze frames' in these movies. As noted by several colleagues,[19-27] the recent triumphs of UED have generated much excitement for the burgeoning field of 'structural dynamics'.

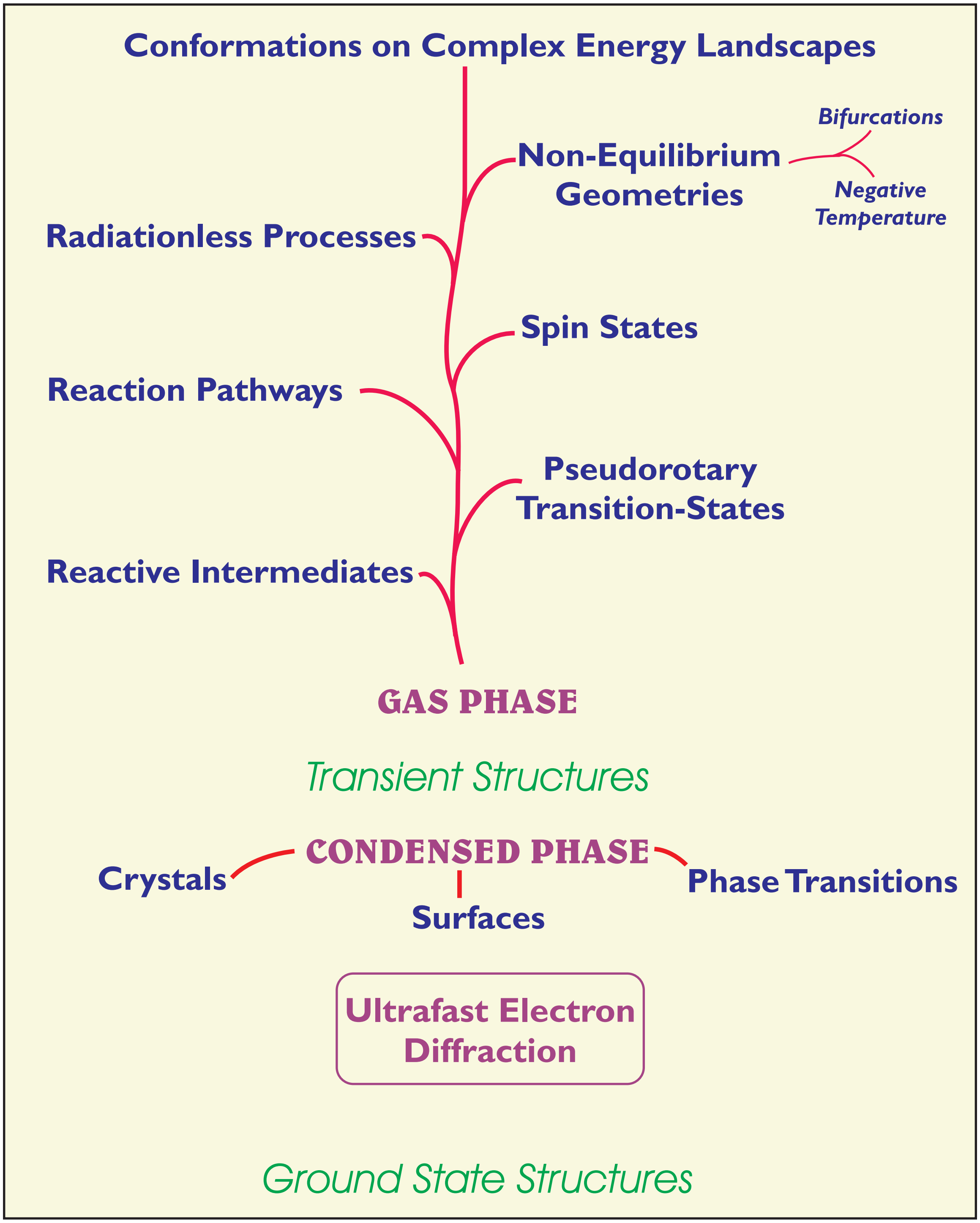

Figure 10-1. The scope of phenomena and concepts elucidated by UED via the determination of ground-state and transient molecular structures.

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