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Preface

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It is hard to overstate the scientific and technological importance of photochemical processes and reactions. The fundamental changes that molecules undergo following absorption of light drives important process in wide ranging fields, from biology to catalysis, photodynamic therapies to molecular machinery, covering the entire spectrum of the physical and life sciences. It is a pillar of chemical reaction dynamics, which itself has a long history that includes developments in spectroscopy, crossed-beam techniques, femtochemistry, and extends to present efforts in ultrafast imaging, with many of these topics reflected in past Faraday Discussions. The overarching challenge facing photochemistry is that it is predominantly a non-statistical process, strongly influenced by the quantum dynamics of the photoexcited system. Complications include exponential scaling with the number of degrees of freedom, strong coupling of nuclear and electronic motion through nonadiabatic couplings and conical intersections, tunneling, interference effects, and ultrafast time-scales. All of this means that a detailed comprehension remains elusive.

In recent years, new experimental techniques capable of monitoring photochemical processes in unprecedented temporal, spatial, chemical, and energetic detail have appeared. This is in large part due to the development of intense-laser techniques, the construction of free-electron lasers such as the XFEL in Europe and the LCLS in the USA, new sources of pulsed electrons, and advanced detection techniques. The challenges associated with making such measurements are manyfold, and analysis of the signals produced is equally difficult due to the often complex interactions of the pump and probe pulses, meaning that the signals cannot always be directly related back to the dynamics measured. This amplifies the complexity, and means experiment alone is not enough to uncover the true dynamics. Progress in experiments is therefore combined with new approaches and important advances in theoretical modeling of quantum dynamics. These have increased the scope and accuracy of the models such that quantitative comparisons between experiment and theory can be made in ever more complex systems and for increasingly complex processes.

Many of these advances are developed by research communities not traditionally concerned with photochemistry. The purpose of the meeting was therefore to gather key participants rep-

resenting the full scientific scope of the topic and to set the agenda for future research. The response from the community was overwhelming, and nearly 120 delegates from 16 countries gathered for this Faraday Discussion on *Ultrafast Imaging of Photochemical Dynamics* at the historical Royal Society of Edinburgh on August 31st, 2016. The format of a Faraday Discussion meeting is ideal for discussions that transgress the many emerging experimental technologies and theoretical techniques, and provides an opportunity to identify the overlap and complementarity of different approaches, while also addressing specific areas of contention and controversy. When reading this volume, it is important to remember that key insights and discussion points are often contained within the discussion segments, and we strongly encourage readers to not only explore the articles but also the associated discussions contained herein.

Looking through this volume, a number of important trends emerge rather clearly. The development of high harmonic sources and free-electron lasers is beginning to give access to pulsed X-ray radiation which opens the door for a wholesale import into the ultrafast regime of an astonishing array of powerful techniques, known for a long time in the synchrotron community. One readily apparent advantage is that X-ray spectra are comparatively uncongested compared to the valence bands. Furthermore, the coherence of lasers increasingly makes non-linear and multidimensional spectroscopies a viable proposition, even in the X-ray domain. Various spectroscopies are also increasingly complemented by ultrafast scattering, via X-rays or electrons, providing a powerful complementary view and more direct access to the time-evolution of molecular geometry. At the same time, the ultrashort pulse durations and high intensities attainable provide alternative routes to structural information and allow us to monitor some of the fastest processes in chemistry through Coulomb explosion imaging and high harmonic spectroscopy.

With such an arsenal of methods, each providing a different view of the dynamics, a combination of techniques is increasingly used in order to attain a more complete picture of the dynamics. Ultrafast imaging techniques are also used to target increasingly complex systems, often including solvents or solid state elements, and dynamic processes that evolve over many different timescales. In terms of theory, it remains important for interpreting experiments but is also used to charter new opportunities, including the potential of light-matter interactions to alter photochemical outcomes. Interestingly, amidst the sustained and ongoing effort towards ever more complete and inclusive quantum

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molecular dynamics simulations, reduced dimensionality models still remain useful. A point made during the discussion was for the community to benchmark one theory against another in order to clearly delineate the strengths and weaknesses of different approximations and approaches.

The experimental and theoretical techniques that are now available are transformative and provide a view of dynamics structure that has previously been inaccessible, with new detection methods only just starting to be explored. Such is the pace of development that it is important that we maintain a collaborative international effort, combining multiple experimental and theoretical approaches to obtain a consistent picture and benchmark their relative efficacy. While the continued development will allow us to follow bond rearrangements directly, in larger molecules and bimolecular reactions, in complex chemical and biological systems and advanced materials, it is crucial that we maintain our efforts to study small molecular systems in an ever more complete manner. The level of detail and precision attainable provides the clearest opportunity to develop the general rules and structural patterns that will provide a "bigger picture" understanding, allowing us to predict the key dynamic processes for wide ranging molecular systems, even if the fine details and absolute timescales differ. Ultimately, it would be fascinating if we could reach a point where it becomes possible to design molecular systems and light fields for a particular function.

We hope this volume serves as an enthusiastic call to arms for the community to not only continue to invent ever better experiments and theory for the study of ultrafast chemical dynamics, but also to uncover any new simplicity that emerges from the increasingly detailed data obtained.

Acknowledgments

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Cote, Claire Springett, Helen Lunn, and Jeremy Allen of the RSC. Please spare an extra moment of appreciation for the editors Helen Lunn and Jeremy Allen, and the effort involved in producing the beautiful volume you hold in your hand.

Shaping the scientific content of the meeting, and selecting among the many strong abstract submissions, would have been difficult without our excellent scientific committee: Jon Marangos (Imperial), Nina Rohringer (CFEL), Olga Smirnova (MBI), and Peter Weber (Brown). Quick-thinking and engaged session chairs are essential for a good discussion, and we were superbly served by the members of the scientific committee together with Dan Neumark (Berkeley), Dwayne Miller (MPSD), Hans Jakob Wörner (ETH), Misha Ivanov (MBI), and Eleanor Campbell (Edinburgh). Possibly the two most difficult *and* important tasks at a Faraday Discussion are to deliver the opening and closing lectures. This was admirably done by our opening speaker Dan Neumark (Berkeley) and closing speaker Dwayne Miller (MPSD). And obviously, without interesting papers of the highest quality, presented by top-notch scientists, and without the active and enthusiastic participation of all delegates, many themselves leaders in the field, this meeting would not have been possible. Thank you.

Finally, we wish to thank the poster prize committee, Vas Stavros (Warwick), Martin Centurion (Nebraska), Carla Figueira de Morisson Faria (UCL), Dmitry Shalashilin (Leeds), and Nirit Dudovich (Weizmann), for selecting the winner (Pedro Nunes, York) among many excellent posters, and Nikola Zotev (Edinburgh) and Andrea Lidberg (Edinburgh) for ensuring that everyone was heard during the meeting. We thank the Faraday Division for their support, and Laser Quantum for sponsorship, and Andrew Turner from the EPCC for an exhilarating exhibit. Finally, we thank the Royal Society of Edinburgh (RSE) for providing an inspiring venue. The RSE counts among its past members James Clerk Maxwell, Paul Dirac, Max Born, and Albert Einstein, and this served as a stark reminder that, as always, we stand on the shoulders of giants, yet look forward to an ever more fascinating future.