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PREFACE

Ultrafast Science: Progress and Opportunities

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An interdisciplinary theme meeting on "Ultrafast Sciences" was held over the period from 31 October-1 November, 2014 at Manipal University under the aegis of the Department of Atomic Energy's Board of Research in Nuclear Sciences. We present in this Special Section a collection of three articles that were adjudged, after peer review, to be worthy of publication from among a number of contributed papers that were presented at this meeting. By way of an overview, some recent examples are presented of ultrafast dynamics explored by physicists, chemists and biologists in the country.

Key Words: Ultrafast Processes; Intense Laser Light; Ultrafast Optics; Photonics; Molecular Dynamics

Ultrafast Science: The Broad Canvas

The term "ultrafast" carries different meanings for workers in different contemporary fields of scientific endeavour. While cosmologists, geoscientists, and archaeologists might regard processes occurring on timescales of a few years or a few decades as being ultrafast events, life scientists are most likely to regard processes occurring on timescales of seconds as being ultrafast. Molecular scientists, including chemists, would surely point out that a prototypical molecule presents them with a variety of ultrafast scales: from nanoseconds for radiative transitions, picoseconds for rotational excitations, and femtoseconds for nuclear motions, to attoseconds for electronic motions within molecules. The origins of the theme meeting on "Ultrafast Processes" lay in the spirit of bringing together scientists from all such disciplines to come together and discuss their "own" ultrafast events. It was hoped that such interactions between scientists from different disciplines would serve to stimulate the generation of new ideas, and the possibility of working out, together, new methodologies that would be of mutual benefit. Moreover, it was anticipated that the diversity of the subject matter of interest in such a meeting would not only attract those working in the areas of the basic sciences but also those who seek applications in physical, chemical, biological and engineering endeavours.

In the following are presented three brief examples of ultrafast processes that have been experimentally explored in a variety of recent experiments conducted by colleagues in India. The topics to have been probed in these experiments cover an extremely wide temporal range: from attosecond dynamics of electrons within molecules to femtosecond-duration nuclear rearrangements within simple triatomic molecules and in polyatomic organics. Such dynamics are accessed using intense, few-cycle laser pulses. In contrast, the third example is an overview of recent experiments that seek to probe the adhesion dynamics of optically-trapped neural stem cells that proceeds on time-scales of ~5 seconds. Such dynamics are accessed with a relatively weak continuous wave diode laser.

Ultrafast Molecular Dynamics: Unimolecular Arrangements

Most experiments in which laser pulses are produced that are only a few tens of femtoseconds long require the use of high intensity laser light that emerges from

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an oscillator-amplifier system. Typical peak intensity values in such experiments are in excess of a few TW cm^{-2}, corresponding to peak optical fields that match the Coulombic fields within molecules. Exposure of atoms to such optical fields inevitably results in multiple ionizations. In the case of molecules also, the intense field inevitably results in field-induced ejection of electrons, leaving behind two or more ionic cores that experience strong Columbic repulsion that, in turn, results in the rupturing of one or more molecular bonds. The fact that strong optical fields readily break bonds was well established in the earliest experiments on the behaviour of molecules in intense ultrafast laser fields. In the course of the last few years or so, experiments have begun to reveal that in addition to the strong optical fields inducing bond breakages in multiply charged molecules, formation of bonds may also be induced (Krishnamurthy *et al*., 2004; Furukawa *et al*., 2005; Okino *et al*., 2006). Such bond formation usually involves a unimolecular process in which intra-molecular migration of protons, or hydrogen atoms, takes place on femtosecond timescales. This has opened possibilities of new chemistry in the strong field regime in the sense that new molecular entities may be formed. By way of illustration, we consider in Fig. 1 the unexpected (and counter-intuitive) rearrangement of H atoms in an H_2O molecule by strong optical fields generated using intense sub-10 fs laser pulses so that H_2^+ is formed (Rajgara *et al*., 2009). This atomic rearrangement is ultrafast: it occurs within a single laser pulse, in a little less than one vibrational period.

Quantum chemical calculations accompanying this experimental work offered indications of an H_2O^{2+} state of the water dication whose asymptotic dissociation limit yields the H_2^+ fragment. Subsequent time-dependent quantum dynamics of this dication have offered support for the experimental findings shown in Fig. 1 (Dharmadhikari *et al*., 2009; Garg *et al*., 2012). Potential energy surfaces (PES) of the ground electronic state of H_2O^{2+} were generated by solving the three-dimensional time dependent Schrödinger equation in Jacobi coordinates for an initial wavepacket (which is the ground vibrational state wave function of neutral H_2O) whose time evolution was followed for many small-time steps on the dication PES. The results clearly showed a proton, generated when the O–H bond undergoes optical field-induced breakage, migrating in the direction of the other H-atom. Such rearrangement is the precursor of H_2^+ in a well-defined spatial region within the PES of the dication. The norm of the wave packet entering this zone was deduced (Garg *et al*., 2012) to be about 1.4% for the $O+H_2^+$ fragmentation channel, in remarkable consonance with the experimental yield (Fig. 1).

Few-cycle pulses of intense 800 nm light also enabled discovery of a time-dependent bond-hardening process in the polyatomic, tetramethyl silane (TMS). Conventional mass spectrometry has long established that ionization of symmetrical polyatmics like TMS does not yield a molecular ion (TMS^+) as unimolecular dissociation into $TMS\text{-}CH_3$ proceeds

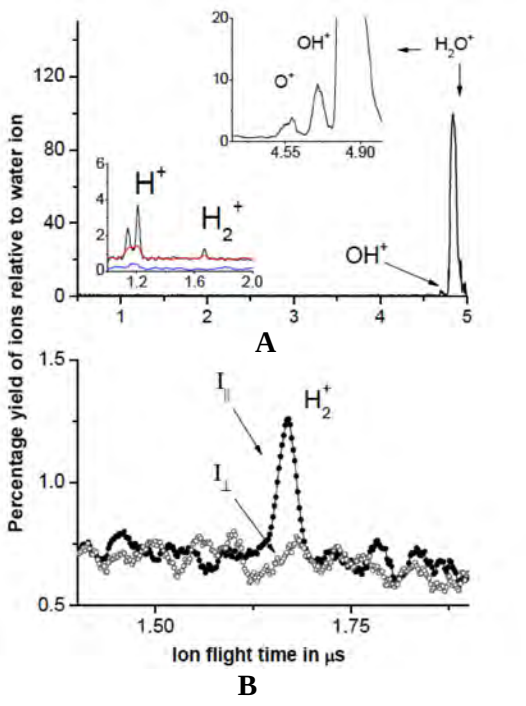

Fig. 1: Formation of H_2^+ upon ultrafast optical field induced rearrangement of atoms within H_2O. (A): Time-of-flight spectrum showing various ion peaks obtained upon irradiation of water molecules by 10 fs long pulses of 800 nm wavelength laser pulses. (B): The H_2^+ ion yield depends on whether the incident laser pulse if linearly polarized along the direction of the spectrometer axis or perpendicular to it. This polarization dependence is a signature of the dynamics occurring within a single laser pulse

very fast. Under a strong field and few-cycle conditions, it has been shown (Dota *et al*., 2012) that this dissociation channel is circumvented because of a time-dependent bond hardening process wherein a field-induced potential well is created in the TMS^+ potential energy surface that effectively traps a wave packet. This results in an effective hardening of the bond. The time dependence of this bond-hardening process has been verified using longer-duration (40 fs, 100 fs) pulses and it has been demonstrated that the relatively slower fall-off of optical field in these longer pulses enables the initially trapped wave packet to leak out, thereby rendering TMS^+ unstable once again (Dota *et al*., 2012).

Ultrafast Molecular Dynamics: Few-Cycle Effects

When the pulse duration is made shorter than about 10 fs, a new parameter assumes importance: the carrier envelope phase (CEP). CEP is a measure of the temporal offset between the maximum of the optical cycle and the maximum of the pulse envelope (see Fig. 2). It has recently become possible to generate 2- or 3-cycle pulses whose CEP can be selected and kept stable, enabling a new class of measurements in which the intensity of the pulse is fixed but the magnitude of the field experienced by the irradiated atom or molecule is controlled via the CEP. CEP effects on the ultrafast dynamics of molecules like CS_2 and atoms like Xe have been carried out (Mathur *et al*., 2013), enabling new insights to be obtained into how non-sequential ionization plays an important role in the overall dynamics that occur in the few-cycle regime. Experiments on CS_2 with CEP-controlled 5 fs pulses have shown, counterintuitively, that fragmentation is enhanced - at the expense of molecular ionization - and that it depends on the instantaneous strength of the optical field (Mathur *et al*., 2013). For instance, fragmentation into S^++CS obtained under conditions of fixed CEP is observed (Fig. 2) to be enhanced by a factor of up to 15 over that obtained with CEP-uncontrolled pulses of the same peak intensity. Moreover, as shown in typical results depicted in Fig. 2, the propensity of different fragmentation channels seems to depend strongly on the CEP. Note how the propensity for formation of doubly and triply ionized parent molecular ions also exhibits some CEP dependence but the overall propensity is actually reduced compared to that obtained with random CEP (Mathur *et al*., 2013).

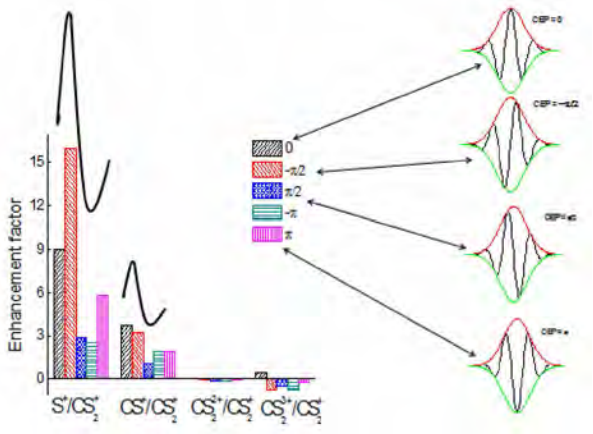

Fig. 2: CEP-dependence of different fragmentation channels that result from strong-field dissociative ionization of CS_2 by 5 fs long laser pulses

"Ultrafast" Dynamics of Cell-Cell Adhesion

Continuous wave, low-power lasers have also been used to probe "ultrafast" processes of biological and biomedical interest. Optical trapping (also known as optical tweezing), used in conjunction with fluid flow technology, has found utility in experimentally dissecting the spatio-temporal dynamics of how neural progenitor stem cells (NSCs) adhere to each other and, hence, aggregate (Ladiwala *et al*., 2012). Stem cells, which are found in many tissues, possess the important ability to self-renew and differentiate into a variety of cell types. Hence, stem cells play a critically important role *vis-a-vis* maintenance of tissue integrity and homeostasis as also in the healingof damaged tissue.Typically, stem cells are cultured as spheroidal neurospheres in a suspending medium. Quantifying and characterizing such cell-aggregates enables one to define and measure stem cell-like behaviour. Until fairly recently, information on how neurospheres and individual neural stem cells (NSC) migrate and aggregate was available on timescales of hours.

Entirely new information has now been obtained on aggregation dynamics by using a tightly focused

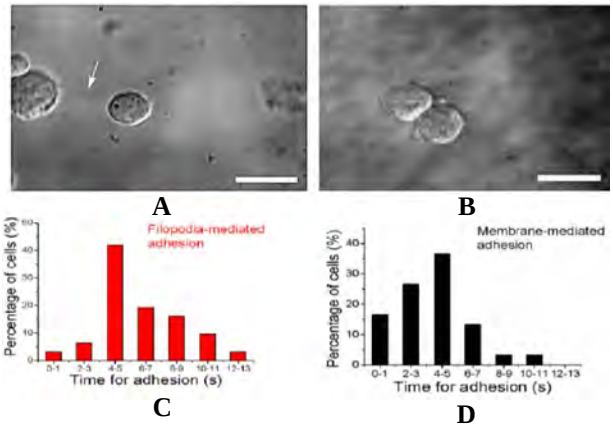

Fig. 3: (A) Neural stem cells joined by a long filopodial bridge indicated by the white arrow and (B) by surface (membrane) adhesion (Ladiwala *et al.*, 2012). The white scale bars denote 10 µm. (C&D) show histograms depicting the percentage of cells undergoing irreversible adhesion as a function of contact time for both filopodia-mediated (C) and membrane-mediated adhesion (D) (Ladiwala *et al.*, 2012)

infrared (1064 nm wavelength) laser beam to optically trap an individual NSC (or a neurosphere) and bring it in close proximity to another NSC (or neurosphere). Ladiwala *et al*. (2012) have recently discovered that a minimum time of about 5s, and most a probable minimum distance of approach of 4-6 µm, is necessary before irreversible adhesion of proximate cells can take place. Such adhesion can be mediated either through filopodia-filopodia interactions or via membrane-membrane interactions. Examples of both type of adhesion are shown in images depicted in Fig. 3. These results have important implications for the neurosphere assay because it establishes that once they aggregate, neurospheresare unlikely to disassemble due to thermal effects or by vigorous shaking, thus indicating that the neurosphere assay, in itself, may not be a valid determinant of "stemness".

Further synergies are expected to be established with researchers in the life sciences. There already exists a rapidly growing list of contemporary research in biology-inspired atomic, molecular and optical physics (Mathur, 2015), and it is anticipated that application of strong-field, ultrashort laser techniques will open newer vistas.

Concluding Remarks

The DAE-BRNS Theme Meeting on Ultrafast Science brought together physicists, chemists and life scientists to discuss various facets of what constitutes "ultrafast" in their respective research domains. The format of the meeting was somewhat unusual in that (i) much more than the usual amount of time was allocated for discussions and (ii) much emphasis was placed on contributed papers presented by young researchers. All contributed papers were allocated prime time for orally presenting a brief (2-minute) summary of their poster as a precursor to intense discussions: the posters were displayed throughout the meeting. Authors of the best among the contributed papers were invited to submit a written-up version, which was then subjected to expert review. The following three papers in this Special Section on Ultrafast Science represent those that were successful.

References

Dharmadhikari AK, Rajgara FA, Dharmadhikari JA and Mathur D (2009) Strong-field ionization of molecules by few-cycle pulses *J Phys CS* **194** 012016-1-8

Dota K, Garg M, Tiwari AK, Dharmadhikari JA, Dharmadhikari AK and Mathur D (2012) Intense 2-cycle laser pulses induce time-dependent bond-hardening in a polyatomic molecule *Phys Rev Letters* **108** 0736021-5

Furukawa Y, Hosina K, Yamanouchi K and Nakano H (2005) Ejection of triatomic hydrogen molecular ion from methanol in intense laser fields *Chem Phys Lett* **414** 117-121

Garg M, Tiwari AK and Mathur D (2012) Quantum dynamics of proton migration in H_2O dications: formation of H_2^+ on ultrafast timescales *J Chem Phys* **136** 024320-1-9

Krishnamurthy M, Rajgara FA and Mathur D (2004) Strong light fields coax intramolecular reactions on femtosecond time scales *J Chem Phys* **121** 9765-9768

Ladiwala U, Basu H and Mathur D (2012) Assembly ingneurospheres: dynamics of neural progenitor/stem cell aggregation probed using an optical trap *PLoS ONE* **7** e38613-1-14

Mathur D (2015) Biology-inspired AMP physics *J Phys B* **48**

022001-1-22

Mathur D, Dota K, Dharmadhikari AK and Dharmadhikari JA (2013) Carrier envelope phase effects in ultrafast, strong-field ionization dynamics of multielectron systems: Xe and CS_2 *Phys Rev Letters* 110 083602-1-5

Okino T, Furukawa Y, Liu P, Ichikawa Y Itakura, R Hosina, Yamanouchi K and Nakano H (2006) Coincidence momentum imaging of ejection of hydrogen molecular ions from methanol in intense laser fields *Chem Phys Lett* **419** 223-227

Rajgara FA, Mathur D, Dharmadhikari AK and Safvan CP (2009) Strong fields induce ultrafast rearrangement of H-atoms in H_2O *J Chem Phys* **130** 231104-1-4.