Photo-Chemical Applications of Phase-Modulus Interdependencies

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November 21, 2018

Abstract

After an accolade to Joshua Jortner, we trace the influences of his Chemistry background in his Physics writings. On the way, we note the richness of Physics in principles (or large-scale laws) and the fact-orientedness of Chemistry.

Next we turn to a recent laser-induced electron-detachment experiment and utilize analytic properties of the developing wave-packet in the (complex) time domain, studied by us previously, to relate the phase of the optimized laser field to its intensity. It is suggested that these results can be used to reduce the labor of pulse optimization in phase-intensity controlled reaction dynamics. Phase-intensity interdependencies are also established in simulated results (obtained with the END-algorithm) for photo-excited hydrogen-molecules.

Short title: Phase-Modulus Interdependencies

Keywords: Scientific Laws, Reaction control, Pulse-shaping, Electron detachment, Optimized laser field

1 Joshua Jortner in Physics. An Appreciation

Few readers will begrudge our saying some nice things about Joshua Jortner, especially from an angle not frequently projected. Praise has been deservedly accorded to him for the quality and importance of his scientific works, for his leadership and for his inspiration to his colleagues. One of us (R.E. or,
in this section, "I" for short) was some time ago (probably in the seventies) a participant and lecturer in one of the Erice NATO workshops. Joshua gave a course there and so did a number of other distinguished scientists, some of whom have achieved leading prominence on the scientific world stage. I conducted a survey among the attendees at the Workshop, mostly postgraduate Physics students, asking them whose course impressed them best, from whom did they learn the most. The list of persons chosen by these young people started with one name and ended with the same. When I pressed them for their reason, they replied that Joshua Jortner talked with a grand sweep, a breadth that opened for them a window to Science, rather than just to the particular subject on which he was lecturing.

In continuation, I wish to delve on a "problematic" aspect of Joshua’s works. A considerable part of these are what most of us would term "Physics subjects". A look at Joshua’s publication’s list reveals that these works appeared variedly in Physics journals, in Chemistry periodicals and in general science forums, which do not qualify as either. The place of the publication does not really matter, what is clear is that many of his topics are comfortably at home in any Physics department.

I would like to discuss this phenomenon (admittedly not unique to Joshua), namely that of someone with a Chemistry background and working in a chemist environment digging into a physics soil to bring up veritable treasures. Or, to use a different metaphor, plucking the fruits of a tree that used to be out-of-bounds, not to say forbidden, to a Chemist. Of course, it is not the ethics of this that I wish to discuss, but whether one can discern in these Physics papers (in their style, in the methodology, etc.) the upbringing of a Chemist.

To make progress, I shall try to draw some distinctions between approaches that are indigenous to chemists and to physicists. Are there such distinctions? On the face of it, there need not be. After all, good science in both disciplines is expected to be honest, open, impersonal, self-critical and objective (all these things being what one likes to subsume under "the scientific method"). Still, there appear to be (somewhat unforeseen) differences, which will be seen relevant to our inquiry.

According to von Neumann, 1 scientific laws are of two kinds. The first kind, called type (A), relate to properties of the constituents of the system under study. Thus they describe or predict properties (such as positions or velocities) of the "bodies" of which the system is composed (e.g., atoms or elementary articles). The second kind of laws, those of type (B), characterize the system as a whole, and do not focus on its parts. A-type laws tend to
be specific in scope, are formal, mathematical. They are empirically based, but are extrapolative and flexible. They tell us that "one may conclude the following as well". In contrast, B-rules tend to be more verbal and less formal and are restrictive in their application. They say: "Only these are acceptable". (One ought to add that in the present understanding one excludes from "scientific laws" axioms, theorems and theories, the latter two being of too limited scope to qualify as laws. One might have called the laws "principles", it being understood that the laws are not only of broad scope, but are also widely accepted.)

It turns out that Physics is very rich in both A- and B-rules. A-rules comprise Laws of Motion of bodies, the Schrodinger equation, the Einstein equation, the Maxwell equations, quarks. B-laws are causality, c-causality or subluminality, positivity of energy, minimal action, the exclusion principle (which perhaps belongs better to A), single-valuedness of wave-function, the correspondence principle, four laws of thermodynamics, Mach’s principle, the principle of frame-independence, the insistence on the simplicity and beauty of theories and possibly others, e.g., Ref. 2. Of course, Chemistry has adopted many of these laws, but without claims of paternity. It has its own rules, too. These are, of the A-types, the laws of multiple proportions, the Lewis laws of structural chemistry, Hückel’s rule, the Woodward-Hoffman rules. Belonging to the B-category one has the atomic "hypothesis" (that matter is composed of molecules and of atoms) and Le Chatelier’s principle. There might be only a few more than these.

One sees from this, as well from the perusal of the scientific literature, that when one is interested in a broad-brushed description, the picture is that Physics (at least as a theoretical pursuit) is primarily principle-laden, whereas Chemistry is more fact-oriented. The former derives its results from a unified description, the latter thrives on diversity. More deductive is the former, matched by more induction in the latter. (It has been said, though vigorously disputed by others such as Harry Lipkin, that the major advances in Physics are essentially theoretical, with experiments playing a confirmatory role.)

In a recent article on the distinguished contributions to Physics by some former chemists and entitled "From chemistry to physics", L. Tisza writes "all three [E.P. Wigner, John v. Neumann and Edward Teller] moved from chemistry that seemed to them an empirical craft, toward a physics based on mechanics that was already penetrated by subtle mathematics". [Tisza either disregards the "principle-richness" of Physics or perhaps insinuates that the three (Jewish-descent-) Hungarians were those who were instrumental
in consolidating it.]

The above distinctions allow us to seek traces of a Chemistry background in Joshua’s approach to physical phenomena and in his distinctive style. But before doing this, let us cite a historical precedent, in which Chemistry and Physics styles of writing are contrasted. The famous chemist, Justus von Liebig, vaunts Michael Faraday’s papers, as follows: "I have heard mathematical physicists deplore that the way Faraday recorded his [results] were difficult to read and understood that they often resembled rather abstracts from a diary. But the fault was theirs, not Faraday’s. To physicists who have approached physics by a road of chemistry, Faraday’s memoirs sound like admirably beautiful music".6

In a less serious vein, we might contemplate the secondary meanings frequently attached to "Physics" and "Chemistry". The former word has the connotation of being deep and fundamental, in the form of, e.g., "the physical reason of this is...". Recently, we have heard a metallurgist saying:"the physics in this is ..." when he clearly meant to say that "the truth in this is ....". In opposition, "Chemistry" has a more vital secondary usage: between two persons it can lead to a happy life ever after, or alternatively, can bring peace and understanding between warring nations.

The "distinctive style" in Joshua’s papers is unmistakable, especially in the Introductions and Conclusions, and it is the same style that impresses one in his lectures. Almost immediately and without warning he immerses the reader in a sea of facts, or in his own words, "in the rich and fascinating world of phenomena".7 The kaleidoscope of phenomena usually includes as enumeration of instances, of effects, being part of a broader phenomenon, of properties, of applications, of varieties of experimental methods and of a list of tasks that await to be done. And it is not just bare facts that are enumerated, but the characterization of each system within a wider context, the ordering of subjects by placing subject x smugly between subjects y and z. The categories are frequently labelled (A), (B), (C), etc. or by equivalent symbols.

Is it unity that the author is taking his aim at? Methinks, it is rather the manifestation of diversification that is guiding him. He is less after establishing a common parentage than the discovering of kinships, seeking to introduce us to a big and independently functioning family and letting us see the role of each individual member in the group. If the above is correct (and the hypothetical factor cannot be sufficiently emphasized), it should leave its imprint on methodology, too. The deductive (and in my view, more Physics-based) approach normally starts with the posing and the solution
of a general problem and takes particular sub-cases in its stride; a more inductive approach places the maximal effort on a specific instance (probably that for which data are awaiting an explanation) and having solved that, reminds us of further instances that have elements in common with the studied one.

It is in this form that the imprints of a chemistry heritage and environment are legible in Joshua’s marvellous works in Physics. How this comes about, has been a concern in the sociology of sciences. It has been proposed, that the norms of the reference group are accepted by the individuals forming part of it. In the phrasing of an eminent sociologist of science, J. Ben David, ”[subject to some reservations] the expectations [in the individual] directed toward a role ... are determined by the institutional definition of the role”.

On more than one occasion we have heard Joshua proclaim the pleasure he takes at theorizing in Physics. ”The physical chemist dines and wines well at the table of Theoretical Physics.” Few have repaid their meal at that table more fully than Joshua Jortner.

2 Background to Reaction Control

The enhancement of a desired end-product in a chemical (or photo-chemical) process through controlled electromagnetic (laser) excitation has been the aim of numerous studies. At least two volumes comprehensively documenting the state of the art have recently appeared, with some articles in them that are of particular interest to the present paper. It emerges that by the shaping of femtosecond laser pulses it is possible to achieve selective molecular excitation leading to a preferred exit channel. (A caveat on impossible pathways has also been sounded.)

A seminal idea in the subject has been that the quantum system under investigation could itself guide (through some automated algorithmic loop) the search for the optimal electric field. In other efforts the relationship between the quantum state and the optimal electric field was brought out in a different form, namely, by explicit formulae giving the latter in terms of (overlaps of) time-dependent wave-functions describing the evolution of the system. It therefore appears from these results that some analytical properties of the molecular wave-function as a function of time (t) are carried over onto the optimized electric field.

On the other hand, some time ago we have investigated the analytic
properties possessed by some molecular wave-functions, in particular of wave-packets formed by vertical excitations between two potential energy surfaces, as functions of the time variable.\textsuperscript{15–16} The root-cause of these analytic properties is the lower-boundedness of the energies entering the wave-packet.\textsuperscript{17–18} This property induces reciprocal relations similar to those in the Kramers-Kronig relations (which are based on causality), but in the present case in the time domain. (The relations are shown below in equation (1) and equation (2)).

These results are applied in the present paper to two recent works involving photo-excitational processes, the first being experimental,\textsuperscript{19–20} while the second is computational, based on the electron nuclear dynamics (END) algorithm.\textsuperscript{21–22} However, before turning to these applications we first describe the mathematical background of our algorithm as applied to an optimized laser field.

3 Reciprocity Relations for an Optimal Field

Let a component of the electromagnetic field vector be written as the complex quantity \( E(R, t) \), with \( R \) representing position vectors inside the molecule. (The field in the present formulation is complex: its real and imaginary parts are associated with the two independent polarizations of the laser light perpendicular to the direction of its propagation.\textsuperscript{9}) For all values of the position coordinates \( R \), let \( E(R, t) \) satisfy as function of the complex variable \( t \), the conditions that it is (a) regular and (b) without zeros in the lower half of the complex \( t \)-plane and that (c) it tends to a constant (\( t \)-independent) finite value for large \( |t| \). (The meaning of these restrictions will be presently discussed.) Then one has the following integral relations:

\[
\frac{1}{\pi} P \int_{-\infty}^{\infty} dt' \ln \left| \frac{E(R, t')}{t - t'} \right| = -\arg E(R, t) \tag{1}
\]

and

\[
\frac{1}{\pi} P \int_{-\infty}^{\infty} dt' \arg \frac{E(R, t')}{t - t'} = + \ln |E(R, t)| \tag{2}
\]

making the logarithm of the field intensity and the phase Hilbert transforms of each other. In the above equations \( P \) designates the principal part of the integral. (For an electric field whose analyticity domain is the upper half of the complex \( t \)-plane, the right hand sides of the above equations change sign.)
To discuss experiments in which the (real) electric field is of the form

\[ E_r(R, t) = F(R, t)\cos(\Omega t + \phi(R, t)) \]  

where the field strength \( F(R, t) \) is positive and \( \phi(R, t) \) is the chirped part (in our terminology, the analytic part) of the phase, one writes

\[ E_r(R, t) = \text{Re} F(R, t)e^{i(\Omega t + \phi(R, t))} = \text{Re} e^{i\Omega t} E(R, t) \]

where \( \text{Re} \) means the real part. If the complex field \( E(R, t) \) thus defined satisfies the conditions (a)-(c) above, then \( F(R, t) \) and \( \phi(R, t) \) are Hilbert transforms, that is to say are connected by equation (1) and equation (2). (The alternative definition of \( E_r(R, t) \), in terms of an imaginary exponent which is the negative of that in the above equations, leads to the same result, owing to the remark in the parentheses at the end of the last paragraph.)

The conditions (a)-(c) are satisfied for a wave packet. To be accurate, one needs to exclude from the overall phase the non-chirped part of the wave packet, since for this the integral in equation (2) is divergent and the formula meaningless; thus, this part of the phase must be taken off the physical phase, before applying the reciprocal equations and then reinserted in the physical quantity. Therefore, if the optimal electromagnetic field mimics the behavior of such wave function, it will also satisfy the reciprocal relations. Our preliminary examination of a field that gives the most efficient transition to an excited state wave packet indicates that this field should indeed have both the same modulus and the same phase as the wave-packet. (There is an analogous result in signal theory: the optimum filter function is proportional to the complex conjugate of the input signal spectrum.)

Condition (b) is included mainly for simplicity. When it does not hold, it can be corrected for. Furthermore when the zeros in the lower half-plane lie far from the real t-axis, their presence is not felt in a limited and frequently physical part of the real time region.

Condition (c) might seem at a first sight to be un-physical, since it requires the field amplitude to be constant (and non-zero) long before and long after the experiment. A natural meaning of this constant is the (temperature dependent) vacuum field intensity. Its value may not be readily available in many cases. This, however, affects the results, as e.g. in the right hand side of equation (1) only by the logarithm of the error committed. (For another, somewhat similarly unexpected, appearance of quantum electrodynamics that is needed to establish consistency, one can call attention to the last paragraph in a landmark paper.)
Figure 1: Potential surfaces (in eV) against $Mn-CO$ distance (in a.u.) (Schematic). Potential surfaces belong, for increasing energy heights at the left hand extremity of the figure, to states A, B and C, respectively. The pump excitation (in the region of 3 eV) from the ground state ($A$) level populates levels in both excited states $B$ and $C$. In a controlled experiment the laser field is so adjusted, as to preferentially populate $C$.

4 Electron Detachment in $CpMn(Co)_3$

A variant of control in photo-chemical processes was proposed in Ref. 25, such that both the intensity and the phase of the optimized laser field were adjusted. Carrying forward this idea, optimization of the electromagnetic field was applied to the carbonyl $CpMn(Co)_3$ ($Cp$ = $\eta^5-C_5H_5$), with a view of obtaining an enhancement of the molecular ion product $CpMn(Co)^{+}_3$, in preference to another fragmentation product $CpMn(Co)^{+}_2$.\textsuperscript{19-20} The latter works gave accounts of a pump-probe experiment in which the exciting field was optimized, so as to achieve an improved ionic yield.

The experimental arrangement in the quoted works, described there in detail, used a laser that sent, in the pump stage, pulses operating at 402.5nm (24844.7cm$^{-1}$) and of about 45 fs duration. The probe pulse consisted of three photons of 805nm (12422.4 cm$^{-1}$) each; these arrived with a variable delay. The optimization was effected by a pulse shaper (operating with 256 pixels), which was capable of simultaneous modulation of the phase (chirping) and the intensity.

Several potential energy surfaces for the carbonyl molecule were shown in Fig. 3 of Ref. 19 as functions of a single nuclear coordinate (the Mn-CO distance). In an adjacent figure (Fig.1), we have drawn schematically only those three potential energy curves that are essential for the understanding of the process. These are the ground state $a^1A'$, named $A$ and the two
states in the excited state manifold, at about 3eV higher, namely $b^1A''$ ($B$), and $c^1A''$ ($C$). It is the enhanced population of $C$ that favors upon a further excitation (the probe) the desired end product (the molecular ion), while population of $B$ will promote upon further excitation of about the same wave-length the competing process: the dissociation of the molecule. Intensities and phases of the optimized electromagnetic fields are shown in the published curves of the above works, in particular in Fig. 1 of Ref. 19. In addition, data values were kindly made available to us through private communication. These data have enabled us to test some analytic properties of the optimal laser field (as function of time), in the manner explained below.

The final conclusion from this test is that in the optimal electromagnetic field there is a significant (though not full) correlation between the phase and the intensity. Theoretically, such correlation would indicate (especially, if confirmed by more extensive tests) that the analytic properties of the evolving molecular wave functions are imprinted on the optimized femtosecond pulse. In this context it should be mentioned that, though the enhancement of unimolecular reactions by an optimal electromagnetic field has been clearly demonstrated by now, details of its dynamics have been in need of better understanding.\(^\text{19}\) On a practical level, the eventual phase-intensity correlation would mean that the optimization of one of these does automatically lead to the optimization of the other. Thus a considerable part of the optimization effort can be spared.

4.1 Optimal pump field

The intensity and phase for the pump pulse which took place in the interval between -100fs and about 50fs, are seen in the first half of Fig. 1 in Ref. 19. However, insomuch that the probe peak follows the pump peak with a delay of about 85 fs and the width of each excitation is also of about this value, the pump intensity curve overlaps the probe curve. This makes the pump part of the experimental curve difficult to consider separately. To make an analysis of the pump curve only, we have taken from the published figure the values of the phase between -100fs and 50fs and then smoothly extrapolated the value of the phase outside this interval to zero. This extrapolated pump-phase curve is shown in the accompanying Figure 2 by a broken line. In the same figure is drawn (by a full curve) the intensity of the pump-pulse, as calculated from the second of the reciprocal relations, equation (2). The curve that this algorithm produces bears a clear similarity to the experiem-
Figure 2: Time (in quarter-fs units) - dependence of the pump-excitation field. Broken line: Phase (in quarter-radians) taken from a section of Fig. 1 (in Ref. 19, but adjusted at both extremities to a zero value. Full line: Intensity (in arbitrary electric field strength units), calculated from the phase through the integral relation in equation (2)
Figure 3: Full-scale optimal phase of the excitation field vs time (in fs). The thin line shows the phase as calculated from the supplied intensity and the formula in equation (1). The thick line gives the phase, optimized in the experiment of Ref. 19.

The flat curve and indicates the *ipso facto* applicability of the reciprocal-relation method. More than this cannot be said about the method, in view of both the theoretical and the experimental uncertainties. The main discrepancy is in the values of the field strength in the wings: in the experiments these tend to zero, whereas the computed strength remains finite (representing the background). The relatively large value is due to the rather flat phase curve. It should be added, however, that when we attempt to apply the same procedure [namely, calculating the intensity from the phase (or vice versa) by the integral relations above] to a different experiment 25, in which the pulse was optimized for a second harmonic generation (SHG) this leads to a complete failure, in the sense that it comes nowhere near the optimized curves shown in Figure 5 of the cited work. 25 That the method works with photo-fragmentation and not with SHG reinforces our supposition that it is the relatedness of the optimized pulse-shape to the developing molecular wave-function that makes the method work.

4.2 Phase-optimized pump and probe pulses

The data values supplied to us spanned the broad range of between -3000 and 3000 femto seconds and thus covered the full duration of pumping and "probing", as well as far beyond. The raw log-intensity data values were inserted in the left hand side of the first of the reciprocal relations, equation
(1), and the phase calculated by integration. The original and calculated curves are shown in Figure 3. Again a significant agreement, though far from perfect in detail, is brought into evidence.

The proposed interpretation of this (admittedly, partial) agreement is as follows: In any actual molecular wave function which arises as the solution of the Schrödinger, the phase and intensity do not vary freely, independently of each other. In particular, this is true of those wave functions which favor electron detachment, or the $CpMn(Co)_{3}^{+}$ exit channel. On the other hand, the generation of any such wave-function by a external pulse of some duration, necessitates some relation between the pulse shape and the wave-function. The hypothesis that is being tested in this work (and to some extent found justified), is that it is the same integral reciprocal relations that hold between phase and intensity of the wave-function, which is also valid for the optimal field.

5 Excitations in Molecular Hydrogen

The formalism named END (Electron Nuclear Dynamics) was designed to give a full description of dynamics of the electron-nuclear system dynamics in molecules, going beyond the Born-Oppenheimer or the adiabatic approximation. A review is in Ref. 26. Of late, the method was applied to study the behavior of $H_3$ (as well as the heavier triatomic $Li_3$), when photon-energy in the range of several electron volts is pumped into the molecule. Descriptions were given of the evolution of nuclear motions, which take place far from the equilateral triangle, equilibrium configuration, of the spin occupancy on each atom and of the amplitudes of excited electronic states (essentially of the HOMO- $\rightarrow$ LUMO excitation amplitudes), all these as functions of time. The time range that was investigated was typically 4 atomic units, or about $10^{-16}$ seconds. An interesting set of computational results were the probabilities $|c^{\alpha}(t)|^2$ and the associated phase shifts $\arg c^{\alpha}(t)$ (Fig. 9 in Ref. 26). The two quantities showed fast oscillations in time. What appears remarkable is that the oscillations between the quantities appear to be correlated, in a manner similar to that predicted by the reciprocal relations. However, in view of the complexity of the curves, as well as of the intricacy of the dynamic situation under study, it was thought inadvisable to try to obtain one conjugate quantity from the other using these curves.

A simpler system is a rotating $H_2$ molecule, whose rotation speed can
Figure 4: Modulus $|c^0|$ and phase of the $HOMO-\rightarrow LUMO$ transition amplitude against time for $H_2$ upon excitation with energy of 4.28 eV. Computed with END. Source: Ref. 27.

be regulated by varying the excitation energy of the molecule. Here again results were obtained by END simulations \textsuperscript{27} for the phase-shifts between spin-up and spin-down amplitudes, and also of the spin-state probabilities, when the diatomic was excited in the 3-4 eV range to induce a $HOMO-\rightarrow LUMO$ promotion. The time dependency of the curve was again oscillatory, with the maxima of magnitudes coinciding with the moments at which the bond was stretched. \textsuperscript{26}–\textsuperscript{27} Moreover, these results were also indicative of temporal correlations between phase and moduli of the type proposed by us. Still, the data were too complicated and minuscule to be useful to us.

A more transparent result was obtained when the phase of the $HOMO-\rightarrow LUMO$ excitation amplitude was plotted and this was compared with the modulus. Figure 4 shows the curves (for an excitation energy of 4.28 eV), as given by the output. It is seen, that the extrema of the moduli coincide with (numerical) maxima of the phase-slope, as well as vice versa. This is a distinctive hallmark of the reciprocal-relations. (Cf. $\sin(t)$ and $-\cos(t)$ are Hilbert transforms of each other). According to F. Hagelberg, the correlation can also be detected in dynamic regions where the phase exhibits a far less regular time dependence than in the time interval shown in the figure. \textsuperscript{27}

The next figure (Figure 5) illustrates the application of the reciprocal relation equation (1) to this system. The "symmetric" curve is essentially the numerical output supplied to us for the excitation modulus, but which has been adjusted in the wings to terminate (at both $t = \pm \infty$) in a very
Figure 5: Synthesized phase for the case of Figure 4. The phase was calculated from the intensity using the integral relation in equation (1) and the modulus values. The modified intensity (the input in the integral relation) also appears in this figure. This is the same as the $|c^0|$ curve shown in the previous figure, but was adjusted and extended at the wings to a small finite value. (Discussed in the text.)

small but finite value. This adjustment is necessary for the convergence of the integrals. The results are only weakly dependent on the value of this limit (to be precise, in a logarithmic fashion). A physical interpretation of the limiting value is the equilibrium value of the excited state population, which is temperature dependent and might be extremely small, but is nevertheless finite. The justification for this is similar to that given at the end of section 3 for the (non-zero) asymptotic value of the electric field intensity.

The computed output is the phase, differentiated from the modulus by it being "anti-symmetric". This is rather similar to the directly computed phase, which was shown in the previous figure.

However, discrepancies are evident in the wings and in the slight, rising slope in the phase. These are connected to the wing-adjustment in the modulus values. A final discrepancy is that the positions of the phase-minima and maxima are interchanged between the directly computed (shown here in the Figure 4) and those that are obtained from the reciprocal relation (Figure 5). The order of the extrema in the latter with reference to the rise or the fall of the modulus is a direct consequence of the lower-boundedness of the energy. On the other hand, a systematic reversal would require a "principle of upper-boundedness", which is difficult to justify. A possible sign mistake in the END data was investigated by their author (Frank Hagelberg) and was found not to be the case. There remains, thus, the need for further clarification.
6 Conclusion

It is very likely that in many instances in the photo-chemistry literature interdependent behavior exists between the phase and the modulus of some quantity. Such behavior may have been noticed in the past, or may not. This paper examines two areas (out of possibly many others), one in the subject of reaction-control and the other in the dynamics of molecules, where the correlated behavior is fairly evident (though not precise in details). We provide a physical rationale for this correlation and give an algorithm (based on the theory of Hilbert transforms) for its prediction. The algorithm can have a practical use of reducing the labor in the optimization of photo-fragmentation protocols.

7 Acknowledgements

Our thanks go to Frank Hagelberg, Cosmin Lupulescu and Ludger Woeste for making their results available to us and for their comments, to Mark Perel’man for discussions and to Hava Nowerstern of the Edelstein Collection for help with the literature.

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