# COMMENTARY

## A New Look at Laser Chemistry

Can lasers control the onset of chaos in energized molecules? Will—at long last—the hopes of physical chemists to use lasers not only to analyze but also to modify chemical reaction pathways come true? What is the correlation between IVR (intramolecular vibrational relaxation) and chaos in molecules? Are the new femtosecond lasers, now available, capable of opening the route to a detailed understanding of these phenomena? What is the status of theoretical concepts? Need one take a new look at laser chemistry? These questions germane to all of chemistry were discussed in a recent workshop "fs infrared multiphoton excitation of molecules" (Max Planck Institute of Quantum Optics, Munich, Germany, July 1993).

Can the rate of an activated chemical reaction depend on the manner in which the energy is provided? The claim of laser chemistry is that is does[1,2] and that one can even use lasers not only to activate but also to control[3] the reaction. Are the new fs lasers, now available, capable of doing this job?

Interestingly enough, the scientific verdict is by no means clear-cut, as reflected in repeated discussions[4] of this topic. The conceptual situation is simpler for so-called "direct bimolecular reactions",[5,6] that is, reactions in which the breaking of the old bond and the forming of the new bond proceed in a concerted fashion and hence occur over times of the duration of a vibrational period ($10$–$10^2$ fs, 1 fs $\equiv$

$10^{-15}$ s). The experimental and theoretical verdict is here quite clear.[5,6] For isolated binary collisions, by selectively exciting certain degrees of freedom of the reactants—those which depend on the nature of the intermolecular forces during the reaction and specifically on the location of the barrier en route from reactants to products—it is possible to enhance the reaction rate above and beyond what can be achieved with the same amount of energy when used as heat. The other side of this coin is also very well documented. Chemical reactions can release energy in a quite specific manner, and this indeed forms the basis for chemical laser action.[1,6,7]

While chemical lasers have long been realized, the complementary aspect, the selective energy requirements of direct chemical reactions, is not yet experimentally easy to realize (but see refs 8 and 9). A possible procedure is to excite the reagents just as they are about to approach. This scheme, which has several other attractive features, has not been realized despite valiant attempts.[10] (For unimolecular reactions there is a similar point of view known nowadays as coherent control.[3])

Issues of both principle and practice arise for the other main class of chemical reactions: that of unimolecular processes leading to isomerization and/or dissociation. Unlike the case of direct reactions, here the stage of formation of the energy-rich intermediate is distinct and separated in time from its eventual evolution to products. This class of reactions is of central interest both because it is typical for polyatomic reactants and because it is particularly suitable for photoselective excitation, the point being that one need not form the energy-rich intermediate by the collision of two smaller reactants, a process known

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(2) Andrews, D. L. *Lasers in Chemistry*, 2nd ed.; Springer-Verlag: Berlin, 1992.
(3) (a) Rice, S. A. *Science* 1992, *258*, 412–413. (b) Neuhauser, D.; Rabitz, H. *Acc. Chem. Res.* 1993, *26*, 496. (c) Bandrauk, A. D., Ed. *Molecules in Laser Fields*; M. Dekker: New York, 1993.
(4) (a) *Photoselective Chemistry*; Jortner, J., Levine, R. D., Rice, S. A., Ed.; Wiley: New York, 1981. (b) *Selectivity in Chemical Reactions*; Whitehead, J. C. Ed.; Reidel: Dordrecht, 1988; (c) Zewail, A. H.; Bernstein, R. B. Real-Time Laser Femtochemistry. *Chem. Eng. News* 1988, *66*, 24–42. (d) *Mode Selective Chemistry*; Jortner, J., Levine, R. D., Pullman, B., Eds.; Kluwer: Dordrecht, 1991.
(5) Polanyi, J. C. *Science* 1987, *236*, 680–686.
(6) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: New York, 1987.

(7) Basov, N. G.; Bashkin, A. S.; Igoshin, V. I.; Oraevsky, A. N.; Shcheglov, V. A. *Chemical Lasers*; Springer-Verlag: Berlin, 1990.
(8) Crim, F. F. *Science* 1990, *249*, 1387–1392. Yang, X.; Wodtke, A. M. *Int. Rev. Phys. Chem.* 1993, *12*, 123–147. Crim, F. F. *Annu. Rev. Phys. Chem.* 1993, *44*, 397–428.
(9) Rubahn, H.-G.; Bergmann, K. *Annu. Rev. Phys. Chem.* 1990, *41*, 735–761.
(10) Brooks, P. R. *Chem. Rev.* 1988, *88*, 407–415. Kleiber, P. D.; Stwalley, W. C.; Sando, K. M. *Annu. Rev. Phys. Chem.* 1993, *44*, 13–35.

as chemical activation. Using infrared laser multiphoton pumping[6,11] one can start with an energy-poor and hence stable compound and up-pump it to the desired energy.

Chemical activation experiments carried out in the 1960s and the IR multiphoton dissociation experiments of the 1970s have satisfied the practitioners that one cannot use energy to selectively drive unimolecular reactions,[12] the argument in essence being that any localized excitation will dissipate over the entire molecule in a time interval which is short compared to the time scale of the chemical change of interest. This is a microscopic, intramolecular analogue of the macroscopic intermolecular energy redistribution which brings systems to thermal equilibrium. It is known as IVR for intramolecular vibrational energy redistribution. The search for selectivity in unimolecular reactions took place at the same period when the mathematical ideas about chaotic behavior in mechanical systems were being assimilated in the natural sciences.[13] The atmosphere was just right for the conclusion that chaos rules out selective processes in unimolecular reactions. Certainly, the experimental evidence was overwhelmingly in favor of this.

Over the years there have been those of us who refused to give up. Chaos, we point out, is a long time phenomenon. In any case, chaos in the multi degrees of freedom systems typical of chemical reactions is quite different from chaos in the idealized two degrees of freedom models which are the simplest to study theoretically. In real systems the energy redistribution will occur in a sequential fashion with different stages occurring on different time scales. In quantum mechanics (which, because of the time–energy uncertainty relation, is a finite time theory) different initial states will evolve differently, etc. We received much solace from the clear-cut observations of selectivity in systems—most notably van der Waals compounds, recently HOD—which contain chemical bonds of rather different frequencies and hence rather different time scales. What was missing, however was the right tool. Are the new fs lasers going to provide what we need? For three days in July 1993 some two dozen of us discussed this question at a workshop organized at the Max Planck Institute for Quantum Optics. Our conclusions were at best tentative and cautious but optimistic. Firstly, however, what are these new fs lasers?

Up to about 1987, fs lasers relied on dye laser technology. They still do, but in addition, new solid-state lasers have entered the arena: Those are using laser materials consisting of paramagnetic transition metal ions in suitable host materials. Often these ions contain just one electron in the d shell (e.g., $Ti^{3+}$) or correspondingly a hole (e.g., $Cu^{2+}$) with the transition frequency being broadened by interaction with the host lattice. This (homogeneous) broadening provides the basis for short pulse generation and amplification. The rest is technology. Find the right combination of absorption bandwidth, stable host material, emission bandwidth/tunability, and lifetime (energy storage). No ultimately optimal combination has been found as yet, but Ti:sapphire at the moment seems to be the best choice and is thus considered to be the workhorse of fs lasers. Its characteristics provide for short pulse operation (<80 fs, even in oscillator–amplifier configurations) with tunability from roughly 700 to 1100 nm and either high rep-rate (80 MHz) or high single-pulse energy (1 mJ).

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(12) Oref, I.; Rabinovitch, B. S. *Acc. Chem. Res.* **1979**, *12*, 166–172. Lupo, D. W.; Quack, M. *Chem. Rev.* **1987**, *87*, 181–216.
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Is this now the definitive approach to mode-specific chemistry? Is pumping and probing with subpicosecond resolution (assuming that the laser fluence as well as frequency (and phase?) characteristics and the pump rates will be sufficient) really accessing the time domain where energy redistribution into unwanted modes (IVR) is at least partially frozen, where the molecular motion is modified by the laser field (not ignoring the fact that the laser has to be tailored accordingly)? This is indeed the hope of those believing in the marriage of laser physics with chemical dynamics. In the specific application of the new fs lasers which operate in the infrared and hence can be used for multiphoton excitation, the aim is to induce large amplitude nuclear motion in order to transform molecules from reagents into products.

We report on the discussion by dividing the topic into three parts: pumping, concepts, and probing, with theory being sandwiched between the operational considerations.

Pumping has to take into consideration that the currently available fs lasers operate in the near infrared, that is, above the fundamental vibrational frequencies. The obvious solution is to pump directly an overtone transition. There is an equally obvious drawback that the strength of overtone transitions ($\Delta v > 1$, where $\Delta v$ is the change in vibrational quantum number) declines exponentially with $\Delta v$. There are, however, a number of compensating factors. Firstly, overtone transitions in polyatomic molecules tend to be localized in specific chromophores (e.g., CH bonds). Hence the initial excitation is inherently selective. Next, overtone transitions are inherently more intense for a molecule which is not in its ground vibrational state. This suggests a two-color pumping scheme. The first laser pumps a fundamental transition (or, even better, its first overtone) so that the second laser is enabled to efficiently pump the state accessed by the first laser into a higher overtone (Lehmann and Scoles, Princeton University). One can also choose such molecules where the high overtones are already within the dissociation continuum.[8] There are several advantages to using a coherent population transfer scheme such as STIRAP,[9] to access the overtone. One can even consider using STIRAP to directly access the continuum (Shapiro, Weizmann Institute), where here, too, the higher frequency of the fs laser is an advantage.

The final point about overtone pumping is that, in computations carried out toward the design of such an experiment (Bintz and Thompson, Oklahoma State University), it was established that overtones can be much more readily accessed by fast pumping. The reason is IVR. With conventional CW (continuous wave) pumping the frequency is well defined, requiring excitation over long durations. There is ample time for the energy of the molecule to diffuse out of the localized region accessed in the overtone transition. This is not so for fs pumping. The separation of time scales with which IVR often takes place (Remacle, Liege University) means that fs pumping can be used to beat IVR, and successfully so.

As important as the pumping scheme is the choice of molecule to be pumped. Here opinions differed markedly. One group (Letokhov, Troitsk Institute of Spectroscopy; Scoles) favored pumping a mode removed from the reaction site. A long, linear molecule would then be best. Others (Reuss, Nijmegen University; Levine, Hebrew University) favored pumping a mode strongly coupled to the reaction coordinate, thereby making the unimolecular reaction look like a direct one.

Much of the discussion of concepts centered about the manifestations and the signature of IVR. Many took part

(Letokhov; Reuss; Domcke, Technical University Munich; Weidenmüller, Heidelberg; Stuchebrukhov, Caltech; Shapiro; Borondo, Madrid; Thompson; Fuss, MPQ; Scoles; Uzer, Atlanta), but it cannot be said that a consensus ensued. Our own reading of the available experimental and theoretical evidence is that IVR can be a sequential process. The number of distinct physical stages will, however, depend on both the initial region accessed and the complementary region. If the later is, of itself, strongly coupled, then only one stage of IVR will be manifested. Often, the variation in frequencies will be such that the initially accessed region is strongly coupled to only a limited range of states. In turn, that larger region is more weakly coupled to a larger region, etc. As the total energy is increased, the number of states into which one can couple will dramatically increase. Yet, this is counterbalanced by the decrease in coupling to very different states. The available, limited evidence is that the two opposing trends do, on the whole, result in an *average* rate of IVR which is only very moderately energy dependent. Since, on the *average*, the rate of unimolecular reactions increases steeply with the total energy, there has to come an energy where the average rate of IVR is no longer higher than the average rate of reaction. Our concern is with lower energies where, on the average, the rate of reaction is indeed the slowest. It is by proper selection of initial conditions that one hopes to be able to obtain a result which, on the average, is exceptional. Such initial states are, we believe, what has come to be known as "extreme motion states",[14] in the terminology of IVR.

An important concept which merits more attention is the nature of the initial state which can be accessed using fs lasers. Unlike CW excitation, fs lasers can excite very localized regions of molecules. In principle, one can almost "pluck" a particular atom. For diatomic molecules, the excitation of what, in quantum mechanics, are localized wave packets has been discussed, sometimes under the term impulsive stimulated raman scattering. Since it is the bandwidth of energy states which can be coherently excited which so clearly distinguishes fs laser excitation, we need to know how one can pump an initial state so as to direct it toward a desired, specific, final fate of the molecule.

At the moment, only qualitative guidelines are available on how to direct the system to a particular exit valley. The easiet answer to this question may be to look for tendencies which nature itself is providing, i.e., for the direction the reaction system wants to go anyway. This is, of course, the way chemists have always worked (and can be related in general to the chemical concepts of self-organization). As to providing some guidelines, there are advantages to

(14) Taylor, H. S. *Acc. Chem. Res.* **1989**, *22*, 263–169.

systems with low barriers, and in practice intuitive concepts relating the initial and final (reactive) states of systems may be invoked (e.g., bending mode excitation favors isomerization, reaction coordinates may be viewed as projections of normal modes onto one coordinate of motion, etc.). Obviously coupling of the initial state to the "wrong" (chaotic) modes would be detrimental, and thus the big task is "to prevent the system from going the wrong way".

The availability of high intensities (up to $10^{19}$ W cm$^{-2}$) from today's lasers makes it tempting to use the laser field to modify the actual forces between the atoms in the molecule. This is the subject of laser control[3] (Shapiro) where the laser not only initiates but accompanies the chemical change. This requires careful tailoring of the laser frequency bandwidth vs time, also known as chirping (Bandrauk, Sherbrooke). Such control has been theoretically demonstrated for triatomics. Ever since the dressing of molecular force fields by those of the laser was conceived in the late 1970s, the experimental realization was always beset by the difficulty of unwanted nonlinear side processes made possible at higher intensities (laser visible multiphoton ionization was indeed discovered while trying to dress the reactants of a direct collision).

Assuming that the short pulse laser excitation has been effective, what type of diagnostics would one employ to analyze the outcome? In principle, there are two distinct approaches: One is to ask for chemical consequences and probe by looking at products; the other, to monitor the time development of the system by laser spectroscopic means. If one selectively populates different energy states of the products, then a limited goal has already been achieved: one has managed to beat the statistics. Ultimately, one does, of course, want to demonstrate chemical selectivity. The deterministic equations of motion of quantum scattering theory allow us to define initial states which will evolve into any predesignated chemical and/or physical state. It remains to be demonstrated in the laboratory that the new fs lasers provide us with the needed tool.

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