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ON THE 1986 NOBEL PRIZE IN CHEMISTRY

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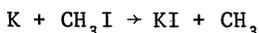
Abstract A review is given of some major trends in the work of the 1986 Nobel prize winners in chemistry, D.R. Herschbach, J.C. Polanyi and Y.T. Lee.

The 1986 Nobel prize in chemistry has honoured three pioneers, who are also current prominent figures, in the field of reaction dynamics : Dudley Robert Herschbach, of Harvard University, John Charles Polanyi, of the University of Toronto, and Yuan Tseh Lee, of the University of California in Berkeley. The works of these three scientists illustrate how the very foundations of chemical reactivity, both in gas phase and more recently in gas-solid interfaces, have been enlightened in the past thirty years by thorough inspection of elementary phenomena such as molecular reactive encounters, evolution of excited isolated molecules, dynamics of adsorbed species. In order to keep this review to a few pages we selected in an arbitrary and personal way a few dozen among several hundreds of papers published by the three Nobel prize winners and their colleagues.

Chemistry is a science of evolution, and at the atomic level the starting point of any evolution is a collisional event : encounter of two chemical species or absorption of a photon by a molecule. Let us start with the former process, which is the hard core of all chemistry.

The first experiments on chemical reactions in crossed

beams propagating in a vacuum concerned KBr formation in the K+HBr reaction and were performed by the group of Sheldon Datz at Oak Ridge, Tennessee, in 1955² and by John Ross and his colleagues at Brown University, Providence, Rhode Island, in 1960.³ One year later, in 1961, Dudley Herschbach, in Berkeley at that time, published his first paper on the reaction



where the beams of potassium atoms and methyl iodide molecules, produced by two ovens, crossed each other at right angles and the potassium iodide molecules were detected by surface ionisation.⁴ The source ensemble could rotate with respect to the fixed direction of the detector, thus allowing determination of the angular distribution of product molecules. A few years later, after D. Herschbach had moved to Harvard University, his student Yuan Lee worked on an apparatus where one of the beams was chopped by a vibrating fork and later a rotating drum, allowing velocity measurements by a time-of-flight technique, and where the detector was now an electron-impact ioniser followed by a quadrupole mass spectrometer.⁵ Later on, Yuan Lee built in Berkeley several setups for the determination of contour maps, i.e. velocity vector distributions, of either atom-molecule^{6,7} or ion-molecule⁸ reaction products.

From the early 60's to the present time the art developed by D. Herschbach, Y. Lee and numerous other workers, mainly in the U.S., in Germany, in Great Britain, and later also in Czechoslovakia, in the Netherlands, in France, in Japan, etc. has been the selection of the quantum states of the reactants and the analysis of the quantum states of the

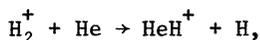
products, in addition to velocity and angle determination. State identification thus has included electronic states, fine structure, as well as vibrational and/or rotational levels, and even alignment of angular momenta. Dudley Herschbach has been particularly interested in the dynamics of angular momentum composition, which his coworkers and he discussed thoroughly in several papers.⁹⁻¹¹ In 1972 he built an apparatus in which highly polar alkali halide molecules produced by alkali atom plus hydrogen halide reactions were deflected by an inhomogeneous electric field, allowing J and M_J selection with the quantisation axis either parallel or perpendicular to the collision plane^{12,9}. An earlier setup had been developed in 1965¹³ and later completed with additional magnetic selection.¹⁴ The results showed that to a large extent the initial relative angular momentum of the reactants is preserved in magnitude and in direction as rotational angular momentum of the product molecule. In addition, reprojection effects have to be considered when the electric field changes direction too fast for the molecular M_J to follow it adiabatically.¹²

The most popular result of a fastly increasing amount of crossed-beam experiments was the demonstration of typical limiting cases of simple bimolecular reaction mechanisms, which we shall list and illustrate with a small set of examples.

(i) The rebound mechanism, in which a more or less knock-on collision leads to back-scattering of the reaction products with respect to reactant initial velocities (except for the atom transferred, which undergoes no change in the direction of its velocity in the centre-of-mass frame), is exemplified by the above-mentioned first reaction studied by Herschbach, Kwei and Morris,⁴ $K + CH_3I \rightarrow KI + CH_3$,

and other reactions of the same kind.¹⁵

(ii) The spectator-stripping mechanism is an $A + BC \rightarrow AB + C$ process where a reactant molecule BC is stripped from atom (or group) B by its collision partner A without any change in the velocity of the remaining moiety C. Apart from a typical pattern in the velocity contour map, this process is evidenced by a rapid fall-off of the cross section when the collision energy is increased up to a point where the AB product molecule acquires enough internal energy to dissociate ; in this way Turner, Dutuit and Lee,¹⁶ studying the reaction

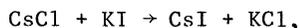


could confirm earlier results of Zdenek Herman *et al.* in Prague¹⁷ and show that the stripping mechanism appeared only when the reacting H_2^+ ions are in vibrational levels $v > 1$.

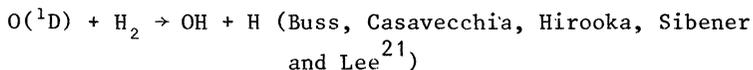
(iii) In the harpooning mechanism an easily ionized atom M (such as an alkali atom) transfers an electron to a molecule XY with a positive electron affinity ; the resulting M^+ and XY^- ions are attracted towards each other by purely electrostatic forces and the reaction (leading e.g. to $\text{MX} + \text{Y}$) then proceeds with a very high cross section ($> 150 \text{ \AA}^2$ typically) since the rate-controlling electron jump may have taken place over a large distance. Studies of such reactions, in particular by D. Herschbach and his colleagues,¹⁸ showed various kinds of angular distributions, each indicative of the most probable angle spanned by the MXY reaction complex before separation of the products.

(iv) Reactions proceeding through a stable intermediate addition complex are revealed by a forward-backward symmetry

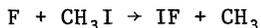
in the velocity contour maps of the final products which testifies that the lifetime of the intermediate complex is long with respect to its rotational period. Either there is forward-backward peaking of the velocity distribution or not, according to the prolate or oblate shape of the complex, as shown by Miller, Safron and Herschbach.¹⁹ That the reactions



studied by the same authors,²⁰ and



belong to this class is not surprising since CsCl and KI are bound through permanent-dipole attraction forces, whereas the insertion reaction of singlet oxygen leading to H₂O in its ground state is a well-expected process. In contrast, the observation by Farrar and Lee²² that the reaction



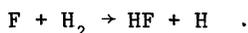
occurs through a long-lived complex, with the consequent stability of the CH₃IF adduct, with an apparently divalent I, was quite unexpected ; Farrar and Lee confirmed its stability by forming this adduct as a final product of the reaction (again in crossed beams)



The CH_3IF molecule however is not stable with respect to $\text{HF} + \text{CH}_2\text{I}$ and therefore this species cannot exist in the bulk phase.

After such limiting cases as the four ones we listed were well documented, a wealth of derivatives of them have been described, with their dependence on the quantum states of the reactants ; sometimes two different mechanisms contribute to a specific cross section ; in other cases a process consists of two steps separated by the migration of an atom ; even more intricate mechanisms are involved in the case of nonadiabatic reactions. We shall limit ourselves to only one more remarkable result.

Long-lived complexes belong to the family of quasi-bound states, where the system, temporarily trapped in a well in the potential hypersurface, is subject to some coupling with the entrance and exit continua. Other kinds of resonant states, having shorter lifetimes, can arise even in the absence of any potential well. These correspond to cases where the quantisation of some vibrational degree of freedom is sufficiently frozen for potential surfaces of individual vibronic states to be of physical significance, and where such a surface presents a well due to the peculiar behaviour of the relevant vibrational frequency in the vicinity of a saddle-point. Such a dynamical resonance was theoretically predicted by Truhlar and Kuppermann²³ and calculated in particular by Launay and Le Dourneuf,²⁴ for the reaction

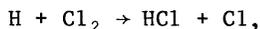


Its first, very delicate, experimental observation was performed by Neumark, Wodtke, Robinson, Hayden and Lee,^{25,7}

who found this phenomenon to occur in the channel leading to the $v=3$ vibrational level of HF.

John Polanyi followed a very different route, in a sense complementary to those of Dudley Herschbach and Yuan Lee. He used gas-flow systems to study simple atom + molecule reactions, monitoring the nascent vibrational distribution, and later the rovibrational states, of the product molecules by infrared emission spectroscopy.

The first reaction he studied in 1958 was



in a simple setup where the chlorine flow met a hydrogen flow after partial dissociation of the H_2 molecules in a Wood's discharge tube.²⁶ In spite of the low resolution achieved at that time a major result was obtained, namely that HCl was produced with an inversion of vibrational population; this led many years later to the design by George Pimentel of the first chemical laser.²⁷

Apparatuses of the next generations developed by John Polanyi and his colleagues had a much better spectral resolution and permitted the study of two successive reactions with different gases,²⁸ then were equipped with liquid-nitrogen or liquid-helium cooling to prevent the observation of emission from vibrationally-relaxed molecules;²⁹ later pulsed molecular beams were used.³⁰ More recently they have used crossed supersonic and effusive beams and detection of the fine-structure states of product halogen atoms by fluorescence induced by a vacuum-ultra-violet laser,^{31,32} in addition to infrared chemiluminescence detection of vibrationally-excited product molecules.³³

During the last thirty years John Polanyi constantly

developed this experimental work on the input and output of translational, rotational, vibrational and electronic energy in a large number of atom + molecule reactions and, in parallel, theoretical work where he used quasi-classical trajectory calculations on model or ab initio potential surfaces. The general goal of this research was to show how the specific features of the potential hypersurfaces control and predict which form of energy is most efficient in promoting the reaction and how the excess energy of the reaction products is shared between the various degrees of freedom.

This enterprise may stem from the tradition which Michael Polanyi, John's father, started with Henry Eyring in the famous 1930 paper³⁴ where appeared the so-called LEP potential surface (London, Eyring, Polanyi) and which was also one of the building blocks for Eyring's theory of absolute reaction rates.³⁵ One may even recall that, due to some approximate calculations, many people later thought that the transition state had some stability. John Polanyi was among the first who rejected this idea³⁶ and kept the concept of the transition state as the "lowest saddle-point",³⁷ i.e. just a mathematical point on the top of the easiest reaction path. He thereafter made a wide use of the fact that the absence of any possibility of thermalisation, and therefore loss of memory, of the transition state opened the way to cybernetics where for each particular event (in classical words) the product state was correlated with the reactant state through the shape of the whole potential surface.

As early as 1959 John Polanyi discussed the behaviours of various types of potential surface for the interpreta-

tion of experimental and theoretical data on 23 exothermic abstraction or association reactions.³⁸ Ten years later J. Polanyi and Wong proposed the well-known rules where the key feature is whether the saddle-point is located in the reactants valley or in the products valley.³⁹ In the former case the reaction is promoted by translational energy and the products appear with excess vibrational energy. In the latter case the reaction can take place only with a vibrationally excited reactant molecule and requires also (in the classical picture) a convenient phase of the vibrational motion ; the product excess energy is mainly translational. In 1981, at the Conference "50 years Dynamics of Chemical Reactions"⁴⁰ commemorating the 1930³⁴ and 1931⁴¹ Eyring-Polanyi papers, John Polanyi reviewed an ensemble of rules, or what he named the "morals" of the effects of various parameters on reaction probability and product energy distribution for three or four-atom systems : mass ratios of the atoms involved, early or late barrier, gradual or sudden barrier, angle of attack, rotation of the reactants, etc. Very recently Mayne, Polanyi and Tully⁴² treated in a similar way the case of nonadiabatic reactions involving two electronic states and discussed how the branching ratio between these states in the outgoing channels and the product vibrational energy distribution depend on the magnitude and location of the avoided crossing in addition to parameters pertinent to adiabatic reactions. John Polanyi's group has shown earlier³² how this electronic branching ratio is dependent on electronic-vibrational transfer between product species in the exit channel, which is related to their own work on relaxation phenomena^{43,33} and also reflects a family tradition.⁴⁴

John Polanyi has been desirous to see the transition

state not only theoretically but also experimentally. In addition to calculations on the expected absorption spectrum of the famous H + H₂ transition state,⁴⁵ he and his coworkers⁴⁶ succeeded in the first observation by emission spectroscopy of a transition state, that of the reaction



This emission of the electronically-excited transition state appeared as wings on the D line emitted by the excited sodium atom produced by the reaction.

In the 1980's an increasing part has been played in reaction dynamics by van der Waals complexes. They appeared both as a natural outcome of the use of supersonic beams, much more intense and monoenergetic than effusive beams, and as a new tool for preparing a well-defined state of a pair of reactants, by exciting or ionising one of the partners of a van der Waals complex.

It is well known that the considerable cooling which accompanies nozzle-beam expansion gives rise to a wealth of van der Waals dimers, complexes and clusters. The first experiments on crossed-beam reactions involving van der Waals complexes were performed by Dudley Herschbach and his colleagues who obtained in 1981⁴⁷ velocity and angular distributions of the XeAr van der Waals complex produced by the reaction



and later studied similar reactions with higher clusters.⁴⁸

Experiments on ion-molecule reactions simulated by the evolution of an ionised van der Waals complex were initiated

by Yuan Lee in a collaboration with the late Bruce H. Mahan and C.Y. Ng. The successive condensation reactions of ethylene ions with ethylene molecules, which are the first steps in the cationic polymerisation of C_2H_4 , were thus investigated⁴⁹ in an elegant way by directly ionising the complexes $(C_2H_4)_2$, $(C_2H_4)_3$, etc. ; this led to a clean thermochemistry e.g. of the reaction intermediates $C_2H_4^+ \cdot C_2H_4$, $CH_2^+(CH_2)_3$, and $CH_3CH_2CH^+CH_2$, up to the products $C_3H_5^+ + CH_3$ or $C_4H_7^+ + H$.

One of the most unexpected applications of van der Waals clusters was a study by Dudley Herschbach relevant to the enigma of solar neutrinos. As is well known, the measurement by Davis et al.⁵⁰ of the solar neutrino flux, using the transformation into ^{37}Ar of ^{37}Cl from a huge tank of C_2Cl_4 , gave a value three times lower than expected. Robert Platzman⁵¹ suggested that there might be an artefact due to trapping of $^{37}Ar^+$ within an $ArC_2Cl_4^+$ ion. A search for this ion by Leventhal and Friedman⁵² using a high-pressure mass spectrometer proved unsuccessful. However Herschbach argued that the reactions leading to $ArC_2Cl_4^+$ in gas phase might be too exoergic for the ion to be stabilised ; Buelow, Worsnop and Herschbach investigated in 1981 the formation of such ions by ionisation of mixed clusters of Ar and C_2Cl_4 .⁵³ They actually found such "bastard" $Ar(C_2Cl_4)_p^+$ ions, but commented that the positive charge should stay on the perchloroethylene molecules and therefore the ^{37}Ar should readily undergo exchange with the ^{36}Ar and ^{38}Ar used in Davis et al's experiment as carriers to extract ^{37}Ar . Thus the enigma was to be solved by other ways.

We shall turn now to the major aspect of half-collision techniques, namely the study of unimolecular reactions.

Numerous experiments on single-photon or multiphoton dissociation of molecules or ions have been performed by the group of Yuan Lee. Some provide answers to questions of high importance to photochemists, other deal with the subtle interference phenomena occurring whenever an excited molecule can evolve towards various continua, and are of interest to physicists.

The isotopically selective multiphoton dissociation of SF_6 , induced by CO_2 laser pulses, was discovered by Ambartzumian *et al.*⁵⁴ Two major questions raised by this process were (i) whether collisions are necessary for the molecule to relax, after each photon absorption, into a state capable of absorbing the next photon, and (ii) whether the dissociation takes place by vibrational relaxation as soon as the required energy content is reached or does the molecule rather absorb additional photons up to a directly dissociating state. Y. Lee and his coworkers answered the first question by showing that the multiphoton dissociation took place as well in a crossed molecular beam + laser beam experiment, therefore under collision-free conditions.⁵⁵ They answered the second question by measuring the kinetic energy distribution of the fragments and showing that it obeys RRKM theory, which indicates vibrational energy randomisation prior to dissociation.⁵⁶

More recently, in April, 1986, Butler, Hintsa and Lee⁵⁷ succeeded in the first demonstration of bond-selective photochemistry, i.e. a photodissociation process where the primary cleavage does not affect the energetically weakest bond. The example was CH_2BrI photolysis at 210 nm, where the only single bond splitting observed is that of the C-Br bond although the C-I bond is far weaker.

Photopredissociation is the phenomenon in which a mole-

cule is excited to a discrete state which is coupled with one or several dissociation continua, into which the system irreversibly evolves. The sign and magnitude of the interference between this process and the direct excitation of the continuum state are apparent from the so-called Fano profile parameter. A remarkable observation recently published by Yuan Lee and his coworkers⁵⁸ was the inversion of the asymmetry of this profile, observed along a Rydberg series, at particular value of the principal quantum number n when H_2 molecules are excited towards Rydberg states predissociating into $H^+ + H^-$. This excitation was performed in two steps : a transition to the $C^1\Pi_u$ or the $B^1\Sigma_u^+$ state of H_2 , by the frequency-tripled radiation of a dye laser pumped by a frequency-doubled neodyme-YAG laser, and the transition from these states to the Rydberg states, by a dye laser again pumped by a frequency-doubled Nd-YAG laser.

The last three examples show how information on events occurring on the picosecond time scale may be obtained through energy-resolved experiments with lasers of much longer coherence time. The same holds for femtosecond events. It was shown by E.J. Heller⁵⁹ and first applied by J.C. Lorquet *et al.*⁶⁰ that the Fourier transform of a high-resolution photoelectron spectrum yields the autocorrelation function of the vibrational motion of the ion. Y. Lee and his colleagues applied this method to acetylene,⁶¹ showing the sharp contrast between the autocorrelation function of the $C_2H_2^+$ ground state, whose vibration is slowly damped by dephasing due to anharmonic coupling, and those of the electronically excited states, which show a decay on the 10^{-14} s scale produced by electronic coupling with other states.

One of the major branches of chemistry, namely hetero-

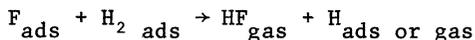
geneous catalysis, was up to the late 70's a technique without any fundamental basis. Experiments on beam-surface scattering and on the photophysics of adsorbed species are disclosing the mechanisms of such reactions.

Since 1980 Dudley Herschbach has been interested in the phenomenon of surface-enhanced Raman scattering. In his most recent work on this topic he investigated with Sandroff and King an electron donor (tetrathiofulvalene, TTF) and an electron acceptor (tetracyanoquinodimethane) adsorbed on colloidal gold particles, and he was able to show that the charge exchange process which takes place in TTF is controlled by the migration of the molecule from a donor-specific site to an acceptor-specific site.⁶²

Photodissociation of adsorbed molecules was studied by John Polanyi and his coworkers, who measured the kinetic energy of ejected fragments by a time-of-flight technique.⁶³ His group also measured rotationally inelastic cross sections in collisions of a supersonic molecular beam on an LiF crystallographic surface.⁶⁴

More recently, J. Polanyi extended the whole problematics of isolated-molecule reaction dynamics to adsorbed species reactions, both by experimental and theoretical investigations. In a recent work⁶⁵ he took up again the study of the $F + H_2 \rightarrow HF + H$ reaction using the infrared luminescence technique, as in his gas-phase work in 1969,⁶⁶ but here the F atoms (produced by a discharge in CF_4) and the H_2 molecules could react not only in the gas phase but also on a surface of CF_4 condensed on a cooled copper wall. The occurrence of reaction on the latter reaction site was evidenced by an enhancement of the infrared emission when the copper cell was cooled under 30 K. The experimental

setup was designed in such a way no light emitted from the wall could be detected, but only the fluorescence of HF molecules returning to the gas phase after occurrence of the reaction



Science has no frontiers, and we shall close this short review by a mention of some recent work of Dudley Herschbach in a field apparently far from reaction dynamics, that of the electronic structure of atoms and molecules. In the past few years he developed⁶⁷ a theory, coming from elementary particle physics⁶⁸ and whose application to atomic structure was suggested in 1981 by Mlodinow and Papanicolaou.⁶⁹ This theory essentially consists in an expansion of the quantum mechanical hamiltonian in powers of the reciprocal of space dimension. It is certainly too early to appraise how fruitful this enterprise will become.

We hope to have shown with those few examples how the 1986 Nobel prize in chemistry honoured three physical chemists whose work and personalities have played an immense rôle in various and rich new fields, where the key problems of chemical reactions have been set and solved at a rapid rate on the basis of an interplay of fundamental reflection and sophisticated technical means.

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