

From alkali flames to automobile combustion — An illustration of the essential role of fundamental scientific research

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Developments in the area of molecular reaction dynamics, starting from the alkali flame experiments of M. Polanyi till the recent laser-induced-fluorescence imaging of the combustion process in an automobile engine, illustrate the essential role of fundamental scientific research.

THE primary aim of basic research is to understand nature, answer curiosity questions of man about himself and his surroundings, and to fulfil a basic need of man, the thinking animal. In addition, there is a need for strengthening basic research from the cultural, technological, educational and political points of view¹. Understandably, a large investment is involved and a high failure rate is implied. But, as J. C. Polanyi^{1a} would put it, 'Some of this wastage has to be tolerated since science is a venturesome activity, and failure is the price we pay for success'. A lot of hard work goes into finding what is usual and what is unusual in nature and thus in establishing an anomaly. It is the latter that leads to discovery. 'Discovery commences with the awareness of anomaly, i.e. with the recognition that nature has somehow violated the paradigm-induced expectations that govern normal science' wrote T. S. Kuhn in his book on scientific revolution². For example, in chemistry, we can point out the pioneering efforts by Berzelius in determining combining (atomic) weights of elements accurately, which led to the construction of the periodic table and also to the discovery of new elements and isotopes³. It is a myth that 'basic' scientists cannot do 'applied' research. The latter is built on the edifice of the former and history is full of examples. In recent times, we can cite the work of basic scientists in the Manhattan Project in the United States⁴. In this country, we can quote the examples of green revolution (increased production of foodgrains) in the sixties and the white revolution (increased production of milk) in the eighties. In this article, I consider an example from the area of molecular reaction dynamics⁵ to illustrate how one thing leads to another and basic research flourishes and eventually bears fruits.

The beginning of today's molecular reaction dynamics research can be traced to the work of Michael Polanyi and coworkers in the 1920s. In his book *Atomic Reactions*, Polanyi⁶ wrote, 'The ultimate goal, then, of the investigation of atomic reactions, is to devise a system of clear-cut rules which will enable us to analyse the more complicated cases of ordinary chemistry; . . . organic chemistry'. From his study of alkali flames we have come a long way to laser-induced fluorescence imaging⁷ of combustion inside an automobile engine.

Polanyi and coworkers carried out the following 'simple' experiment. They allowed vapours of sodium to come from one end of a glass tube and chlorine gas from the other, let them react to form sodium chloride as a deposit in the middle of the tube, and, from its distribution, determined the reaction rate constant to be equal to $14 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The rate constant predicted from collision theory is $0.6 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The observed rate was an order of magnitude higher than that predicted by collision theory. This was clearly an anomaly as, for all gas-phase reactions studied till that date, the observed rate was less than or equal to the collision-theoretic rate. It implied that there was reaction before collision! Polanyi and coworkers explained this unusual result by proposing a harpoon mechanism: the alkali atom (M) 'throws' its electron off to the halogen molecule (X_2) to pull the resulting X_2 towards the newly formed M^+ to yield an MX in a stretched configuration (and of course an X) (see Figure 1). Naturally, such an MX would be vibrationally hot!

It took nearly 30 years (the son had to grow up!) before vibrationally excited species formed in a chemical reaction could be studied. When Cashion and Polanyi⁸ at the University of Toronto mixed a stream of hydrogen atoms with chlorine gas, they could record the infrared chemiluminescence (IRCL) from the freshly formed hydrogen chloride molecules, indicating that the molecules were vibrationally hot. Following the reports on the maser, Polanyi⁹ described the conditions under

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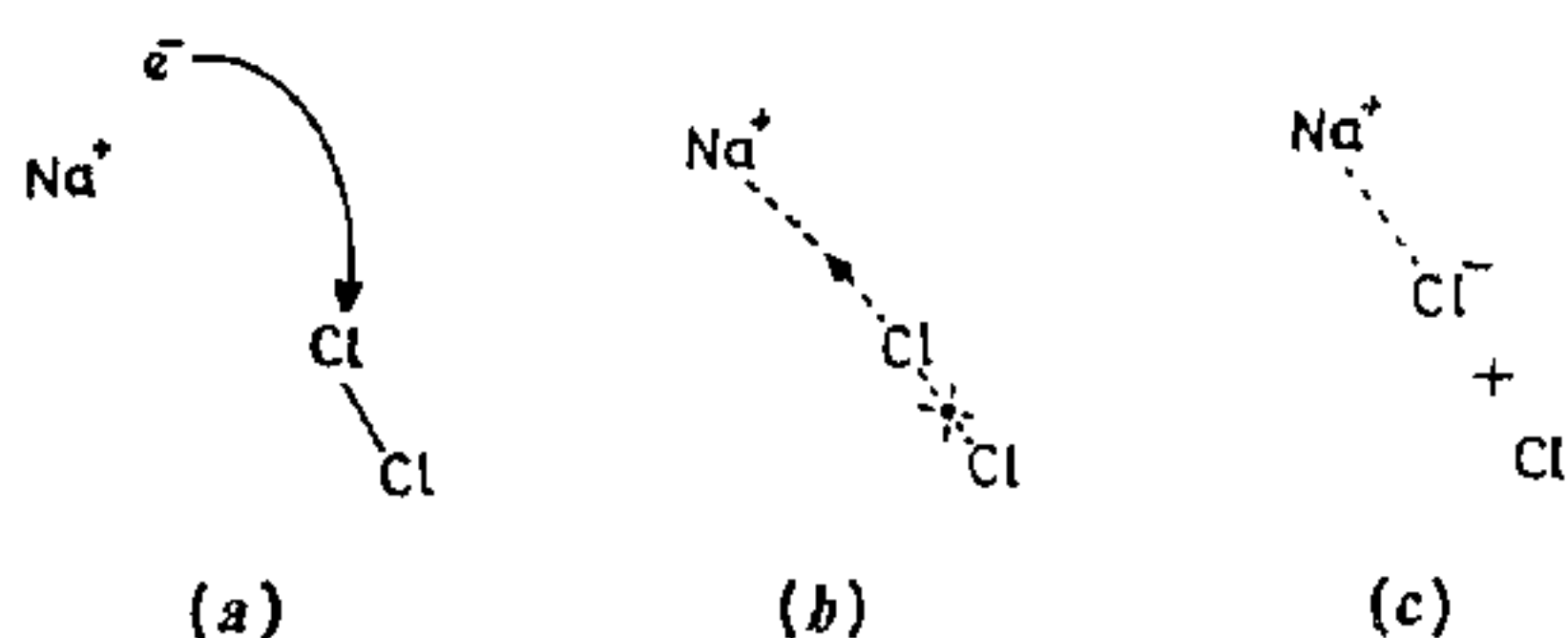


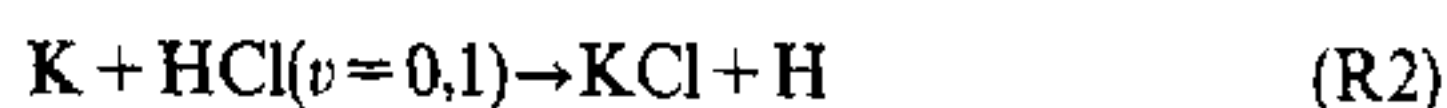
Figure 1. Schematic illustration of the harpoon mechanism: (a) Na 'throws' its valence electron, (b) Na⁺ pulls Cl₂, and (c) Na⁺ . . . Cl⁻ is vibrationally hot.

which an infrared maser (iraser) could be formed. At this point, it is worth mentioning that when he, along with the chairman of his department, discussed with the university lawyer about applying for a patent on the idea, they were told that it was not worth the trouble. Polanyi and coworkers went on to use the IRCL technique to understand the nature of chemical interaction¹⁰. They determined the product vibrational and rotational energy distribution for



and several other exothermic reactions. Using the principle of microscopic reversibility, Analuf *et al.*¹¹ showed that the results implied that, in the reverse, endothermic direction, vibrationally excited reactants would react much faster than their counterparts in the ground vibrational state. Also, using the vibrationally hot product in one reaction as a reagent for another (pre-reaction concept), Polanyi and coworkers demonstrated that there was a large *vibrational enhancement* in substantially endothermic reactions. Using fourier-transform infrared technique, they were able to establish *rotational inhibition* in some reactions. Along with their experiments, Polanyi's group also carried out detailed computer simulation studies to unravel the mysteries of the forces operative in a chemical reaction.

In a parallel development, Kasper and Pimentel¹² constructed the first working infrared chemical laser. Several infrared chemical lasers have been constructed since and have been used to study and understand the working of chemical lasers and also to study *selectivity* in chemical reactions. I would like to mention in particular some of the classic work done by Brooks and coworkers at the University of Houston. In 1971, using an HCl chemical laser to excite vibrationally HCl molecules in the reaction



Odiorne *et al.*¹³ showed that HCl(*v*=1) was 100 times more reactive than HCl(*v*=0). In 1979, Dispert *et al.*¹⁴ demonstrated that, for the *v*=1 state of HCl, increase in rotational excitation resulted in a decrease in the reaction cross-section.

In the early seventies, many chemists started using infrared chemical lasers and the powerful carbon dioxide lasers which had become readily available by then to investigate their effect on reactions involving polyatomic molecules; some started using them as 'substitute for Bunsen burner'¹⁵. More importantly, the question that was raised was: Can we do bond-selective chemistry? For example, in CHFClBr, can we selectively dissociate the C-F, C-Cl, C-Br or the C-H bond? The speculative answer was that we could, using multiphoton absorption *provided* there was no energy randomization. In their study of infrared laser photochemistry of SF₆ for example, Letokhov and coworkers¹⁶ found evidence for dissociation of an S-F bond, meaning that about 30 photons were being absorbed per molecule. Researchers in the field had anticipated that with intense laser-light sources, there would be multiphoton absorption. But an absorption of 30 photons per molecule was beyond anybody's expectation. Soon it was found that multiphoton absorption/dissociation (MPA/D) was selective; so selective that different isotopomers (isotopically substituted molecules) responded differently. It was possible to selectively dissociate ³²SF₆ and not ³⁴SF₆ or vice versa. The implication for isotope separation in general and (²³⁵,²³⁸U) in particular was profound. Several laboratories across the world started studying MPA/D in UF₆ and the details, for obvious reasons, are kept a guarded secret. The commercial viability of isotopic enrichment in other elements—boron, carbon, chlorine, bromine, sulphur, etc.—using MPA/D has already been established.

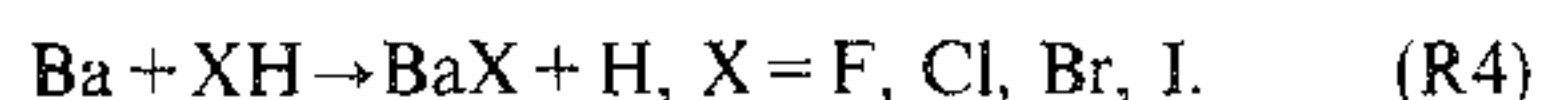
From the fundamental point of view, energy randomization in large molecules has been a subject of intense research for several decades. Reddy and Berry¹⁷ investigated, using overtone excitations, the effect of different amounts of vibrational energy in the C-H mode on the isomerization.



and found that the reaction rate increased with increase in vibrational energy content, in accordance with the prediction of (RRKM) unimolecular reaction rate theory, which assumes energy randomization in a polyatomic molecule. In the case of allyl isocyanide (CH₂=CHCH₂NC) isomerization, on the other hand, different overtone excitations, $\delta\mu_{\text{CH}}$ (methylene), $\delta\mu_{\text{CH}}$ (olefinic CH) and $\delta\mu_{\text{CH}}$ (olefinic CH₂), led to different isomerization rates, implying *mode selectivity*. Different schemes for successful mode-selective chemistry have been proposed since¹⁸.

Zare and coworkers¹⁹ started using the technique of laser-induced fluorescence (LIF), in which a continuous-wave dye laser is tuned to different vibrational states of a molecule in its ground electronic state and fluore-

science from the excited state is collected in order to determine the product vibrational state distribution in reactions like



The method has since been used for a variety of systems under a variety of conditions. It has also been used to detect and monitor trace amounts of pollutants in the environment. But perhaps the most dramatic use of the technique was demonstrated recently by Andresen and coworkers⁷ who 'imaged' the combustion process inside an automobile engine by monitoring the ro-vibrational state distribution of OH radicals in space and also as a function of time (Figure 2).

I have tried in this article to illustrate the essential role of fundamental scientific research using examples

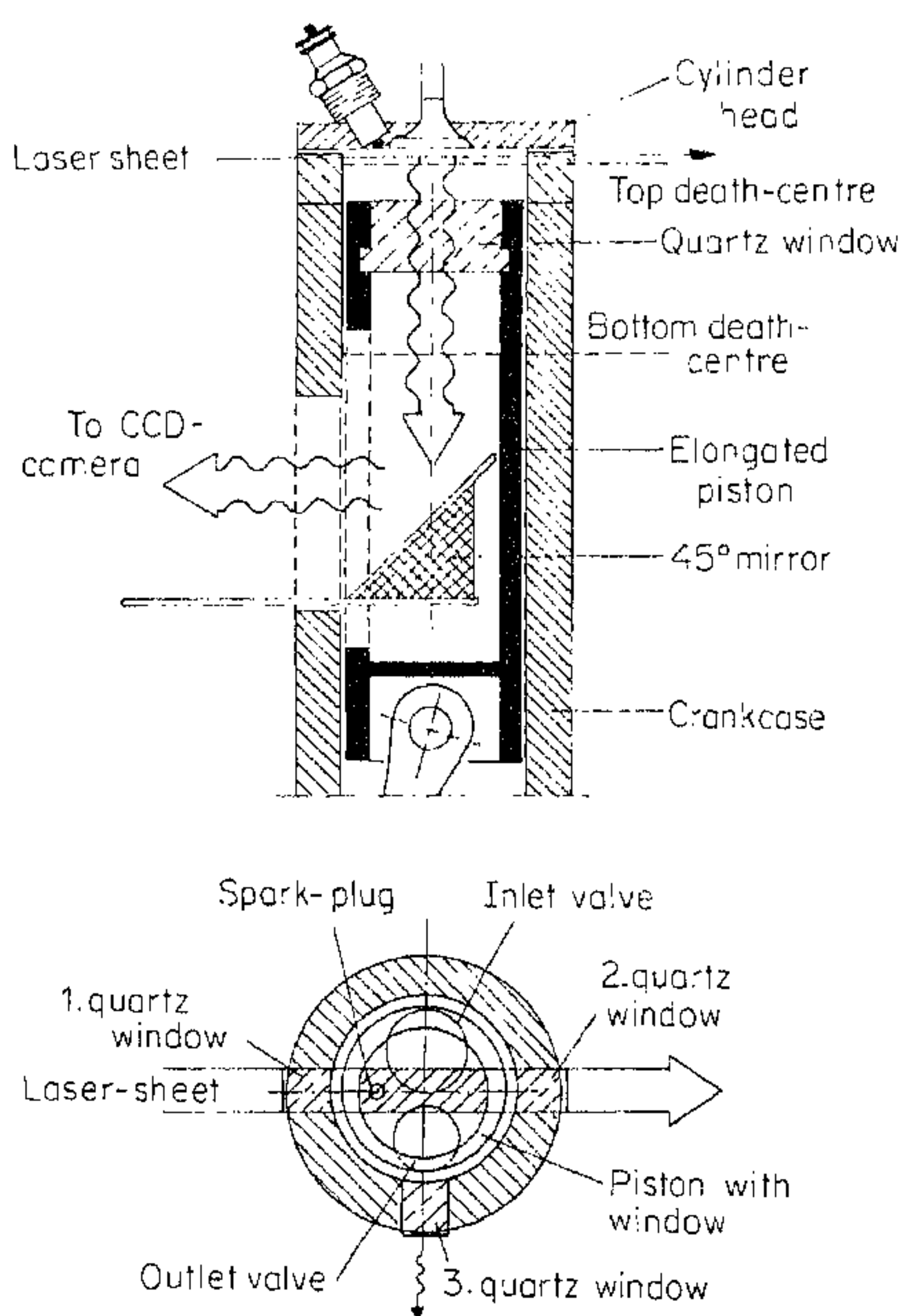


Figure 2. Experimental set-up for laser-induced-fluorescence imaging of combustion.

from the area of molecular reaction dynamics. It would be worth pointing out that some of the research cited above required neither huge investments nor high technology and could have been done in this country at about the same time. But it was not. The reason seems to be lack of 'scientific culture'. A country that could boast of Raman, Bose, Saha and the like in the early part of this century has not come up with men of similar stature in the later part in spite of substantial investment in terms of money and manpower. Having built the 'infrastructure', we need to cultivate creative science in the country.

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