

REVIEW

Reminiscences of the Physical Chemistry Research that I Took Part in at Dalian in the Days from 1951 to 2000[†]

Cun-hao Zhang*

*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China***I. FROM THE INSTITUTE OF PETROLEUM TO THE INSTITUTE OF CHEMICAL PHYSICS, THE CHINESE ACADEMY OF SCIENCES**

In December 1950, a few weeks after I returned home from a two-year graduate study in the US, I met in Beijing Professor Da-yu Zhang, then director of the Dalian Institute. He kindly invited me to pay a visit to Dalian. On that first sight of Dalian, I began to like the city, the institute, the research career that soon tied me up with synthetic liquid fuels research and, above all, the upright and simple character of Professor Zhang, as a tutor and as a leader of science. So I declined all previous offers in Beijing and came to Dalian right away to work under him.

Since its inauguration in 1949, the Dalian Institute was focusing overwhelmingly on heterogeneous catalysis, especially catalysis related to synthetic liquid fuels, including hydrogenation of CO, various types of reforming, and high pressure hydrogenation of coal tar and shale oil. This was the strategy that Professor Zhang laid for the institute. For that cause the Institute changed its name to Institute of Petroleum in 1954. Beginning in early 1951, I spent eight years on the Fischer-Tropsch synthesis catalyst and process development. The existing fused iron catalyst that was then under extensive evaluation in western countries suffered from serious carbon deposition during the CO hydrogenation reaction. Nan-quan Lou, Shan-yun Wang, Yu-sheng Tao and I adopted the US Bureau of Mines practice to treat the freshly prepared iron with ammonia, a "nitriding" process, that effectively eliminates the carbon deposition. Further, we added both fused and impregnated alkali to the nitrided catalyst as an effective promoter to achieve a higher selectivity. For every cubic meter of CO+H₂, the yield of oxygenates, ethylene and C₃⁺ hydrocarbons reached over 200 grams, a record high. We even set up and ran a pilot plant [1], and in the late fifties, a demo plant. But eventually the process was shown economically infeasible for the moment. In retrospect, it was really a pity that we did not try to develop a new generation of catalysts with a view to

further improve the selectivity. Along with the discovery of Daqing oil field and other Chinese oil reserves, and the founding of the new research institutes under the Ministry of Petroleum, our institute finally chose to give up the name Institute of Petroleum and in 1962 changed to a new name, the Dalian Institute of Chemical Physics (DICP).

II. SOME RESEARCH TOPICS WITH MY CLOSE COLLABORATORS ON MESOSCOPIC CHEMICAL PHYSICS IN THE NINETEEN SIXTIES

Frankly speaking, in the early sixties I knew very little about chemical physics. Now I understand that for the immediate past half century, chemical physics deals principally with nano- or subnanometers in length scale and femtoseconds in time scale. In the half century earlier than that, however, chemical physics was typically related to micrometers in length scale and micro- to nanoseconds in time scale. Naturally, these latter topics, of which combustion was a fashionable one, should now be categorized into the arena of mesoscopic chemical physics. Nevertheless, combustion and gaseous detonation, while not considered a part of modern theoretical chemistry, still belong to the realm of physical chemistry. So, in 1964 my collaborators Guo-he Sha and Rong-yao Zhang started working on shock tube kinetics and gaseous detonation, with graduate students Zheng Xu and Cheng Shang-guan. In the nineteen sixties, our lab was indeed very poorly equipped, with no spectrometers, no modern electronics, etc. Nevertheless, we made significant progress until the Cultural Revolution came in 1966, when all these were demolished. Here I wish to illustrate with two examples under the category of mesoscopic chemical physics that I took part in, viz., (i) theory of composite propellant combustion [2,3] and (ii) laser supported detonation waves [4].

My first example deals with the burning rate theory of solid composite propellants. In the late nineteen fifties through early sixties, the technology of large solid propellant rockets was developing very quickly. Concurrently, the theory of linear burning rates for composite propellants became a hot topic in the early sixties. A composite rocket propellant consists of an oxidizer, mostly ammonium perchlorate, and a binder/fuel, essentially a polymeric material that on heating undergoes pyrolysis to give a gaseous fuel. Up to 1963, there

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*Author to whom correspondence should be addressed. E-mail: zhangch@mail.nsf.gov.cn

were over two dozen relevant theories. Independently, the theory for both premixed and diffusion flames had been developed by previous authors to a nearly perfect stage so as to allow each to be incorporated into the whole picture. However, theories for composite propellant combustion were still either physically unsound or mathematically too crude. In 1963-1964, my collaborator, Guo-zhong He made considerable progress in building a multiple layer flame theory [3] that encompassed the advantages of almost all previous theories. His theory served to incorporate (i) an oxidant-rich flame as a result of the decomposition of tiny particles of ammonium perchlorate with (ii) a diffusion flame resulting from further burning of the pyrolysis products with the oxygen-rich gas. In view of the high ambient pressure under which the propellant burns, the flames become so thin that both of them can be very well described by an impulse function. Thus, the mesoscopic structure of a burning composite propellant is reasonably quantified as follows [2]: a premixed flame is lying about one micron above the burning surface and, as the overall energy conservation criterion requires, a second diffusion flame has to lie about 10 microns further away. Next, by using refined models for the premixed and diffusion flames, Guo-zhong He worked out the analytical solutions [3] to correlate the burning rate with all key parameters for the propellant and combustion.

The second example represents our study in 1983 on the laser-supported detonation waves (LSD) [4]. When a laser pulse with an intensity above 10^7 - 10^8 W/cm² irradiates a solid surface, a plasma ignites and propagates at hypersonic speed, typically $M \sim 40$, from the surface towards the incident beam, forming an LSD wave. Before our work, LSD has been studied by a large number of authors, typically with CO₂ lasers. Starting from scratch, Guo-he Sha led a small group to build in 1982 an e-beam initiated, H₂/F₂ chain laser with an output energy of ~ 30 J/pulse and with a ~ 0.8 μ s pulsewidth. As the LSD velocity exceeds 1×10^6 cm/s, previous authors had to resort to costly streak cameras for its measurement. In contrast, Guo-he Sha chose the spatially resolved luminescence method and was able to quantify the velocity by using only a couple of low grade oscilloscopes and two PMT's. Despite that the method is simple and cheap, we achieved an accuracy of ~ 10 per cent, enough to attest the theory. We also built a ballistic pendulum to measure the impulse imparted by the laser pulse onto the target. A target chamber is used so we could vary the ambient pressure and ambient gas composition. Altogether, Sha was able to obtain a good correlation between pertinent parameters and to give an adequate interpretation of the LSD waves by a 1-dimensional gas detonation theory, except the chemi-exoergicity in the gas detonation has to be replaced now by the laser energy input. This investigation also helped us to elucidate the structure and nature of the LSD wave. For example, the impulse imparted on the target originates principally from the pressure

exerted by the LSD wave, while the contribution from the ejectants accounts for only a very minor extent.

III. DOUBLE RESONANCE SPECTROSCOPY AND DYNAMICS OF MOLECULAR ENERGY TRANSFER

Towards the mid-nineteen eighties, the interest of Sha and I shifted to molecular spectroscopy and dynamics, finally entering the realm of the orthodox chemical physics. At that time, our colleagues Nan-quan Lou and Guo-zhong He were already pioneering in China molecular dynamics research with beam-gas and crossed beam machines. Moreover, Qing-shi Zhu came from the Qinghai Salt Lake Institute to Dalian to give a series of seminars on modern molecular spectroscopy, which aroused extensive interest among not only the graduate students, but also the senior staff. Besides, he started in the eighties the first high resolution spectroscopy studies (on silane and methane) in China at DICP, which lasted for almost ten years before he moved to USTC in Hefei. His FT-IR works on spherical and symmetric tops won much appreciation from Professor Zheng-kai Wu, senior spectroscopist in the country.

So Sha and I chose to develop novel laser spectroscopic techniques that aim at unraveling the structure and dynamics of excited molecular species, specifically the technique of optical-optical double resonance multiphoton ionization (OODR-MPI) [5]. OODR spectroscopy, first developed by Field *et al.* [6], is characterized by running two transitions between three energy levels. It is governed by stricter selection rules, resulting in a drastic reduction in the complexity of the molecular spectra. Moreover, multiphoton excitation by tunable lasers in the optical region allows access to high-lying electronic states of molecules, which would have required very expensive tunable vacuum ultraviolet light sources. Ionic detection competes favorably with photon counting; with a little care and a number of simple tricks, the former is capable of providing both higher signal-to-noise ratio and higher sensitivity. These features combine to make OODR-MPI an extremely versatile spectroscopic technique, whose potential has not yet been fully exploited.

In 1985, Jin-chun Xie, then my graduate student, devised a variant of OODR-MPI known as ion-dip spectroscopy (IDS) [7] to obtain rotational spectra of very short lived predissociating species. Specifically, our endeavor dealt with a short-lived species, NH₃A¹A₂' with a lifetime around 100 femtoseconds [7]. Each rotational line is broadened to several tens of wave numbers because of the short lifetime, and in conventional spectroscopy there is always complete overlap of the rotational lines with the adjacent ones to form a diffuse spectrum. With IDS, we first performed the three-photon excitation to pump ground state NH₃ to the C' state, and from there, another photon brought it to the ionization continuum. Then with the first laser

locked to a specific rovibronic transition $C'(v', J') \leftarrow X$, we scanned a second laser to bring about the stimulated emission $A(v, J) + h\nu \leftarrow C'(v', J')$. IDS is in essence an ionic detection version of the stimulated emission pumping (SEP) first developed by Kinsey, Field *et al.* [8]. Whenever the second laser hit such a transition, the $C'(v', J')$ species would have an additional depletion channel besides the usual one going to ionization, which caused a dip in the ion signal.

Although IDS lines of iodine were obtained earlier [9], the lines in our spectra for NH_3 were much more pronounced, owing to the fact that the A state predissociates fast enough to make the reverse process $A \rightarrow C'$ very unlikely. We worked out the selection rule that for each $C' \leftarrow X$ rovibronic transition, the follow-up $A \leftarrow C'$ transitions could be at most three, and these were readily assignable. It was also simple to determine the line center positions. Accordingly, a "composite" rotational spectrum could be constructed, and the rotational constants B and C and the band origins could be obtained by least square fit [7]. Noting that for many molecules, the first excited electronic state is a short predissociating state, our method should work for many of them, as long as their lifetimes are longer than a few tens of femtoseconds.

As we found the vibrotational levels of the NH_3 A state with IDS, we proceeded to explore the B state by straight double resonance $B \leftarrow A \leftarrow X$ [10]. Most of this work was performed by Xiao-nong Li, Bo Jiang *et al.*, in 1990-1991, then my graduate students. Because B is a degenerate electronic state, Jahn-Teller splitting can occur as a result of coupling between the electrons and nuclear vibrations. If the levels were purely vibrational, the symmetry should be E . Owing to the Jahn-Teller effect, however, each of these levels splits into E and A . Thanks to the OODR technique, we actually observed this splitting by distinguishing the vertical bands of PQR structure, which is characteristic of the E symmetry, from the parallel bands of the PR structure, which is characteristic of the A symmetry. By these means, we successfully studied the rotational Jahn-Teller effect, assigned each type of band and evaluated the vibronic coupling parameters [10].

We went a step further to study the Jahn-Teller-induced Fermi Resonance [10]. Previously, Fermi resonance was studied only in the ground electronic state and was allowed only between the vibrational modes of the same symmetry. Now, because of the Jahn-Teller splitting, new types of Fermi resonance become allowed between the vibrational levels of the excited electronic state B . This Jahn-Teller-induced Fermi Resonance is termed non-adiabatic Fermi resonance and is in some cases governed by novel selection rules.

Since 1984, my collaborator, Guo-he Sha led a team to apply the technique of OODR-MPI to the study of molecular dynamics. By this technique, which may also be grouped into the widely used pump-and-probe technique, we were able to study collisional energy transfer

processes in considerable detail.

In a static sample cell, we vary the sample gas pressure as well as that of the collider, usually a rare gas, so that only single collision is experienced within the interval of the laser pulsewidth.

First, a laser, usually of subrotational resolution, is locked to a specific quantum transition, e.g., $\text{CO } A(v, J) \leftarrow X$. Then, as a second laser scans, the ion signal spectrum shows in addition to the parent lines a host of daughter lines as a result of collisional energy transfer. From the intensity ratio of daughter to parent lines, absolute energy transfer cross sections are computed, usually to an accuracy of ~ 10 per cent. Furthermore, propensity rules can be inferred [11]. Mostly with $\text{CO } A^1\Pi$ and $e^3\Sigma^-$ states as the model species, we investigated several "subrotational" processes, including (i) rotational energy transfer (RET) with doublet parity change or conservation [12], (ii) RET within a triplet (for example, $F_2 \rightarrow F_1, F_2$, or F_3) [13], (iii) singlet-triplet intersystem crossing [14], (iv) rovibronic energy transfer between $\text{CO } A$ and $\text{CO } X$ [15], (v) collisional angular momentum reorientation of $\text{CO } A$ by helium [16], and (vi) collisional quantum interference within CO or Na_2 singlet-triplet mixed states [17-20]. The elucidation of many of these items were possible only because of the experimental accuracy that we reached by taking a great deal of care in the experiments.

The last item, i.e., collisional quantum interference, was Sha's most favorite topic and could be the first instance of the discovery of quantum interference in the nonradiative transitions, or between two de Broglie waves. A transition phase angle θ_{ST} is established to quantify the quantum interference effect with considerable success. Let the transition probabilities for pure singlet and triplet states be $P_{jj'}^{\text{S}}$ and $P_{jj'}^{\text{T}}$, respectively. Physically, θ_{S} and θ_{T} represent, respectively, the phase changes during the singlet and the triplet transitions. Defining a transition phase angle θ_{ST} by $\theta_{\text{ST}} = |\theta_{\text{S}} - \theta_{\text{T}}|$, our model gives the $J \rightarrow J'$ transition probability as the sum of 3 terms:

$$P_{jj'} = c_j^2 c_{j'}^2 P_{jj}^{\text{S}} + d_j^2 d_{j'}^2 P_{jj}^{\text{T}} + 2c_j c_{j'} d_j d_{j'} (P_{jj'}^{\text{S}} P_{jj'}^{\text{T}})^{1/2} \cos \theta_{\text{ST}}$$

where the c 's and d 's are mixing coefficients. In comparison, previous authors described only two extreme cases. Thus, Freed and Gelbart's model [21] contains only the first two terms of the above equation, implying that the two complex integrals are always out of phase by $\pi/2$, making $\cos \theta_{\text{ST}} = 0$, while Lefebvre and Field's derivation [10], despite comprising three terms, suggests $\cos \theta_{\text{ST}} \equiv 1$, i.e., $\theta_{\text{ST}} \equiv 0$, signifying the two integrals are always in phase. So both of them fail to embody all actual cases. On the other hand, we did the fittings for θ_{ST} from the experimental cross sections and made quantum mechanical computations as well. The experimental and theoretical values of θ_{ST} we obtained agreed very well with each other. Altogether, we gave ample theoretical justification and experimental evidences for

the interference in collision-induced energy transfer between singlet-triplet mixed states.

In addition, as the deputy director (1979-1983) and the director (1986-1990) of DICP, I worked with my colleagues in fostering young talents in science, besides making endeavor to strengthen both basic and applied researches. Our goal has in part been fulfilled as evidenced by the burgeoning of a whole new generation of young scientists from the Institute, e.g., Can Li, Xin-he Bao, Xue-ming Yang, Tao Zhang, Zhong-min Liu, Han-fa Zou, Yu-qi Jin and many others. I then left Dalian to serve for two terms (1991-1999) as the president of the National Natural Science Foundation of China, during which, among various undertakings, I succeeded in setting up the State Distinguished Young Scholars Fund. Up to the present, close to two thousand scholars around the country have received this grant. As a result, the Fund already helped to invigorate and update Chinese science in the past dozen years.

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