

Chapter 19

STIRAP: A Historical Perspective and Some News



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A very brief outline of what STIRAP is and does is followed by the presentation of the sequence of experiments, which started some 50 years ago, the visions developed and experimental efforts undertaken, that finally led to the development of STIRAP.

1 What Is STIRAP?

Stimulated Raman Adiabatic Passage (STIRAP, [1]) is a process which allows efficient and selective population transfer between discrete states of a quantum system, in its simplest form shown in Fig. 1. Level 1 is initially populated. The goal is to transfer all of that population to level 3. In most cases of interest, a direct one-photon dipole coupling between levels 1 and 3 is not possible. Therefore, one needs to invoke an intermediate level 2, often in a different electronic state. The characteristic and initially surprising feature of STIRAP is that the quantum system needs to be exposed first to the S-laser, which couples initially unpopulated levels. When the intensity of the S-laser is reduced, the intensity of the P-laser, which provides the coupling to the populated level, rises. If the switching-off of the S-laser and the switching-on of the P-laser is properly coordinated and the so-called adiabatic condition is fulfilled [2] nearly 100% of the initial population in level 1 will reach the target level 3 without ever establishing significant population in level 2. The underlying physics is interference of transition amplitudes, which—in the adiabatic limit—prevents population in level 2. Therefore, loss of population during the transfer process through spontaneous emission does not occur or is much reduced.

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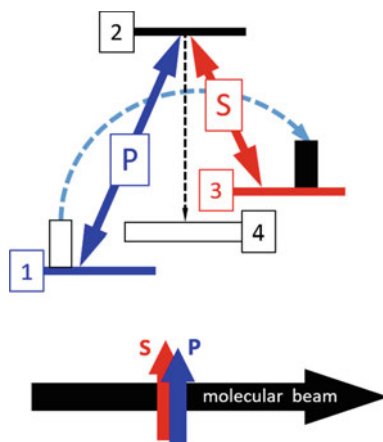
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Fig. 1 The upper part shows a three-level system with the S- and P-lasers, coupling the levels 2–3 and 1–2, respectively. Level 4 stands for all levels that can also be reached by radiation from level 2. The lower part shows the geometric arrangement (S-before-P) for population transfer within particles of a molecular beam

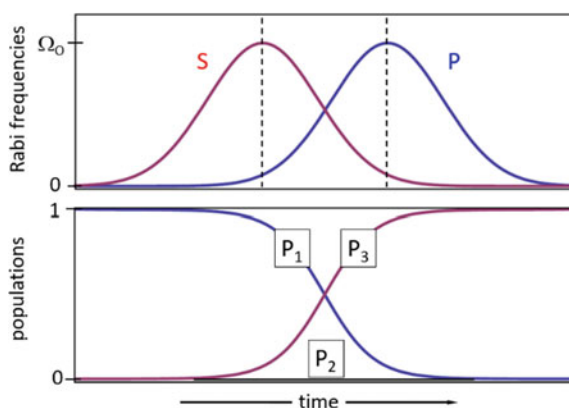


The S-before-P sequence, called “counter-intuitive pulse sequence” in the early days, can be implemented either by suitably delayed laser pulses when applied to molecules in a gas cell (Fig. 2), or by spatially shifting the parallel axes of continuous lasers when population transfer within particles of a molecular beam is to be realized, as shown in the lower part of Fig. 1. It is the directional flow, which guarantees that a given molecule experiences a time variation of the coupling between levels as shown in the upper part of Fig. 2.

Another important feature, namely the robustness of STIRAP, made the scheme popular in many laboratories for applications in a wide and diverse range of quantum systems (see Sect. 6). Robustness means that a small variation of the S- or P-laser intensities or their time-delay does not reduce the transfer efficiency.

The original publication, reporting the main features of STIRAP and its theoretical foundation [1], was followed over the years by a number of review articles, e.g. [3–6]. The wide range of applications is documented in [7].

Fig. 2 The upper part shows the STIRAP-sequence of laser interactions with the quantum system (S-before-P). The variation of the Rabi frequencies, which determine the coupling strength between levels, is shown. The lower part shows the corresponding flow of population P_x from level 1 to level 3 (see Fig. 1). In the adiabatic limit no population is deposited in level 2



This article does not offer a detailed discussion of the physics of STIRAP. It describes, in the format of a memoir, the background, the vision, the various steps and the systematic plan followed, which finally led to realizing how a complete and robust population transfer between quantum states can be achieved. This work concludes with the presentation of a short list of topics or problems which benefited from the application of STIRAP. Although STIRAP has also been applied to many types of quantum systems, including a polyatomic molecule, the specific discussions and comments that follow relate mainly to diatomic molecules.

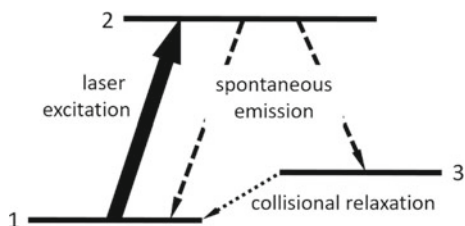
2 Background and Motivation

The deep roots of STIRAP reach back in time more than 50 years. The topic of my diploma thesis (submitted in early 1968) was the dynamics of photodissociation of some polyatomic molecules, using a classical pulsed high pressure discharge source [8]. After completion of that work my response to the question whether I wanted to continue this kind of experiments was a determined “no”. I stated the reason: such work would very soon be done with lasers. In 1968 lasers were known for only 8 years.

Lasers did indeed play a central role in my PhD thesis, completed in early 1972. That work led to one of the very first applications of lasers to collision dynamics. The topic of the thesis emerged from spectroscopic work in sodium beams done by W. Demtröder while visiting R. N. Zare in Boulder [9]. In my work home-built Argon-ion lasers were used to excite a single rovibronic level (v', j') in the B-state of sodium molecules in a cell with rare gases added. (Here and below I use the traditional convention from spectroscopy: a single prime marks a level in an electronically excited state, while a double prime refers to a level in the electronic ground state.) Atom-molecule collisions induced transfer of population to neighboring rotational levels. That transfer was monitored by observing collision-induced spectral satellite lines. The pressure dependence of the intensity of those lines allowed the determination of rate constants. Of particular interest was the difference between rotational energy transfer to levels ($v', j' + \Delta j$) and ($v', j' - \Delta j$). The first paper on this topic [10] appeared in print only a few months after J. Steinfeld had published similar studies for I_2 , also involving a laser [11]. Because the transferred energy was small compared to the mean kinetic energy, the observed difference of the rate constants for excitation and deexcitation processes with the same $|\Delta j|$ (called propensity) was unexpected. It was later explained through a detailed analysis of the wave functions involved [12].

While doing Ph.D. work, I learned about the then very popular molecular-beam technique through close contact with students working in a neighboring laboratory. The offer to continue academic work at the University of Kaiserslautern, founded in 1970, triggered the plan to combine molecular beams and lasers in future research. In early 1973, while carefully studying a paper by R. Drullinger and R. N. Zare on optical pumping of molecules [13], in particular their discussion of excitation and relaxation

Fig. 3 The level scheme relevant for optical pumping of molecules in a gas cell showing laser-excitation, spontaneous emission and relaxation via collisions



pathways (see Fig. 3), I realized that the relaxation path after laser excitation and spontaneous emission back to the initially pumped level would be missing in the collision-free environment of a molecular beam. Thus the entire population of a specific thermally populated rotational level j''_{pump} could be removed. Controlled by Franck-Condon factors and optical selection rules, only a very small fraction of the laser-excited molecules would return to levels near j''_{pump} by spontaneous emission. This consideration led to the crossed beams arrangement as shown in Fig. 4. Particles scattered under the angle ϑ into the level j''_{probe} were probed by laser-induced fluorescence (see Fig. 5) while the pump laser would periodically switch off the population in level j''_{pump} . Most of the experiments involved levels in $v'' = 0$.

With the pump laser turned off, all thermally populated levels may contribute to the scattering into the probed level. With the pump laser turned on, the contribution from the pumped level would be missing. The difference of the scattering signal with pump laser off and on isolates the scattering rate from the level j''_{pump} into the level $j''_{probe} = j''_{pump} + \Delta j$ ($\Delta j > 0$ and $\Delta j < 0$ possible) under the scattering angle ϑ which is determined by the position of the narrow entry slit of a rotatable detector.

The molecular-beam laboratory for doing such experiments in Kaiserslautern (built after my post-doctoral work in Berkeley with C. B. Moore on laser-induced

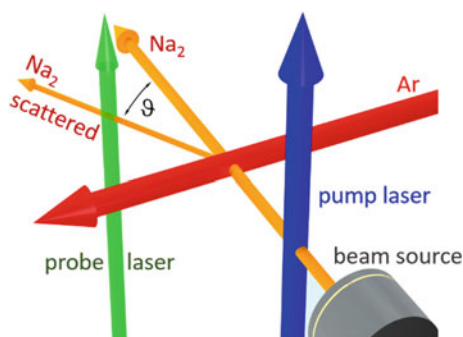
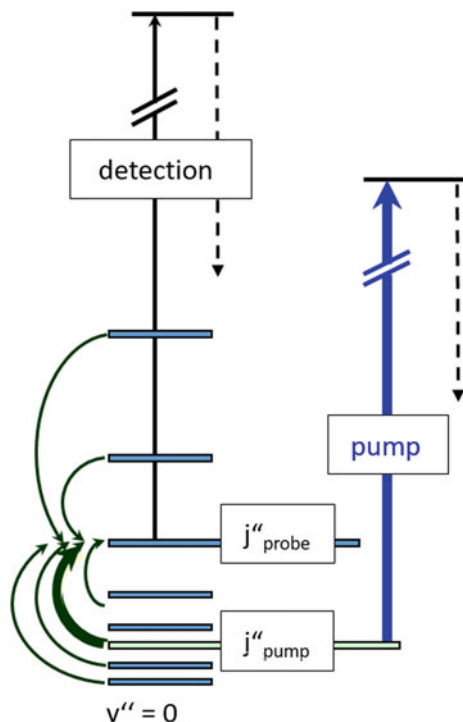


Fig. 4 The crossed beams arrangement for the study of state-to-state angle-resolved inelastic scattering, with a Na_2 -beam, an Ar-beam, the pump-laser and a laser beam for monitoring the flux of particles scattered under the angle ϑ into the quantum state j''_{probe} . The device for collecting the fluorescence induced by the probe laser is not shown

Fig. 5 The level scheme relevant for the scattering experiment as shown in Fig. 4. For further discussion, see the text



chemistry [14, 15]) had several innovative features. The entire apparatus was designed from the very beginning with the central role of lasers in mind. By design, some components, which were traditionally considered absolutely necessary, were not even included. In particular hot-wire detectors for detecting alkali atoms or molecules were replaced by lasers. Equally relevant: the mechanical flexibility of the detector, required for measuring angular distributions, was provided through the use of single-mode optical fibers in combination with a new design for efficient collection of laser-induced fluorescence [16]. A prerequisite of this work was a careful state-resolved characterization of the molecular beam [17].

Figure 6 shows what is most likely the very first AMO research laboratory with an optical-fiber network implemented, only a few years after Corning had manufactured the first Germanium doped single mode fibers. The photo shown was taken in 1977. Several lasers were connected to a number of experimental stations in different rooms with single-mode optical fibers donated by the fiber-research laboratory of Schott/Mainz. It was the late colleague Walter Heinlein from the electric engineering department of my university who introduced me to the relevant researchers in that laboratory. None of the optical components needed for coupling laser radiation into and out of fibers were commercially available. The photo was first shown in public at the ICPEAC conference 1979 in Kyoto. This photo triggered much more interest than the content of the related scientific presentation, namely the first laser-based

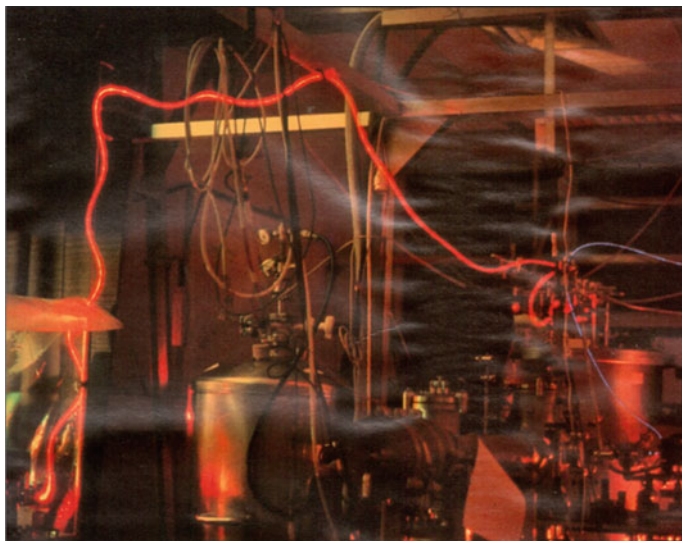


Fig. 6 The photo from 1977 shows what is probably the first laboratory with an optical fiber network installed, for flexibly connecting a number of lasers with various experimental stations

angularly resolved state-to-state energy transfer cross section [18]. The laser-based approach to molecular-beam scattering proved very successful. It led to a series of experiments yielding fully resolved state-to-state differential energy-transfer cross sections, with “rotational rainbows” being a prominent feature, see e.g. [19, 20], including even *m*-selectivity [21].

3 The Vision and the Challenge

Motivated by the success of the work mentioned in Sect. 2, I was considering in the late 1970s to use in my future work laser-based molecular state selection for laboratory studies of collision processes with relevance to atmospheric chemistry. It was known that chemical reactions and photodissociation processes in the higher atmosphere may lead to highly vibrationally excited molecules. However, little was known about how such vibrational excitation would change reaction-rates. The problem, though, was that the state-selection by optical pumping as described above works only for thermally populated levels. In a molecular-beam environment the levels $v'' \gg 1$ of interest are not populated. In order to use an approach similar to the one of Sect. 2 and shown in Fig. 4, one needs to efficiently and selectively populate a single rotational level in a highly vibrationally excited level. “Efficiency” was needed to

realize a sufficiently high flux of excited molecules for scattering studies. “Selectivity” was crucial because reaction rates may sensitively depend on the vibrational level.

Further considerations, which are documented in my Habilitation Thesis submitted in late 1979 [22], led quickly to the conclusion that a direct one- or multi-photon excitation of a $v'' \gg 1$ level in the molecular electronic ground state would not be possible. The transition moments for high-overtone excitation are too small. Extremely strong laser pulses would be needed. At such high laser intensity many detrimental multi-photon excitation and ionization paths would make the approach inefficient. For homonuclear molecules the relevant transition moments are zero anyway.

Thus, it was straightforward to conclude that any efficient transfer scheme must invoke an auxiliary third level, most likely in an electronically excited state. On- or off-resonance Raman scattering, π -pulses or a sequential chirped adiabatic passage process were candidates. However, any process that drives the population through a level in an electronically excited state would suffer from unavoidable loss of population through spontaneous emission. Such processes would not only reduce the transfer efficiency to the target level; even worse, spontaneous emission would spoil selectivity because levels adjacent to the target level would also be populated. Off-resonance Raman scattering would reduce or avoid spontaneous emission, but the optical selection rules would prevent reaching levels $v'' \gg 1$ from thermally populated rotational levels in $v'' = 0$. Neither would the use of π -pulses allow reaching the goal, because the pulse area of the radiative interaction (roughly speaking: the product of the mean Rabi frequency $\Omega = \mu E/\hbar$ and the pulse duration, with μ being the transition dipole moment and E the electric field of the laser radiation) needs to be precisely controlled. Such transfer would not be robust. The transfer efficiency would depend very sensitively on small changes of relevant parameters. It would be different for different m -states within the rotational level. A sequence of two π -pulses would therefore allow the transfer of only a small fraction of the population of molecules in a given j level, also because the condition for efficient transfer would be satisfied only for a tightly restricted number of trajectories of the molecule across the laser beam. A flux of molecules sufficiently high for scattering experiments would not be achievable.

Soon after reaching these conclusions the process of stimulated emission pumping (SEP) was proposed [23], which turned out to be very powerful for some collision dynamics experiments [24]. However, in most cases, the transfer efficiency did not exceed 10%. Thus, the problem was temporarily put aside with the hope that a new idea or a new inspiration would come along.

4 An Intermediate Step: The Molecular Beam Laser

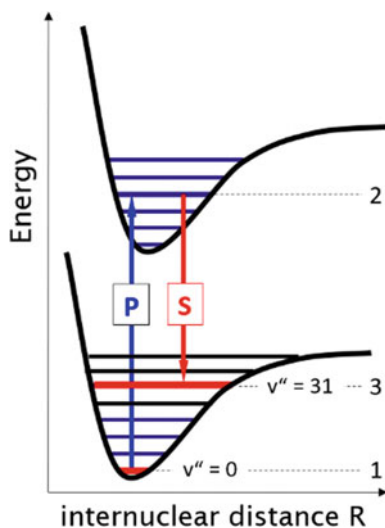
The new inspiration came through discussions with B. Wellegehausen and after reading his papers on optically pumped lasers with alkali dimers in a heat pipe (length

of the order of 10 cm) serving as gain medium [25]. In that work it was shown that high gain can be realized for transitions from levels in electronically excited states (populated by laser-pumping from thermally populated levels) to many high lying vibrational levels (see Fig. 7) in the electronic ground state. For many such transitions lasing was observed with a power of the pump laser as low as 1 mW. My quick back-of-the-envelope calculation showed that the gain in a molecular beam about 1 cm downstream from the nozzle would be even larger, despite the small extension of only a few mm. The reason is that the population distribution over low lying rovibronic levels in a supersonic beam is characterized by a temperature on the order of 10 K [17] rather than the ≈ 750 K in a heat pipe.

That conclusion quickly led to a preliminary design of a cavity around the vacuum chamber supporting the molecular beam. Figure 8 shows the second generation of such a cavity. An essential difference between a molecular-beam laser and a heat pipe relates to the relaxation process of population reaching the lower laser level (level 3 in Fig. 7). Such relaxation, removing continuously population from the lower laser level, is needed to allow continuous laser operation. In a heat pipe relaxation is dominated by collisions. In the molecular-beam, however, it is the directional flow that continuously transports new molecules in low-lying thermally populated levels (level 1 in Fig. 7) into the region of the laser cavity and at the same time removes molecules in level 3 from the cavity. These latter molecules do not experience further collisions. They remain in the highly vibrationally excited level and are available for collision experiments. Rotating the birefringent filter allows choosing which vibrational level is populated.

It was a very crucial moment when Uli Hefter and Pat Jones tried for the first time to get the molecular-beam laser going. It rarely happens that such experiments work at the first try. In this case it did happen on July 28, 1981. The cavity was aligned

Fig. 7 The level scheme relevant for an optically pumped dimer laser, using molecules either in a heat-pipe or in a molecular beam



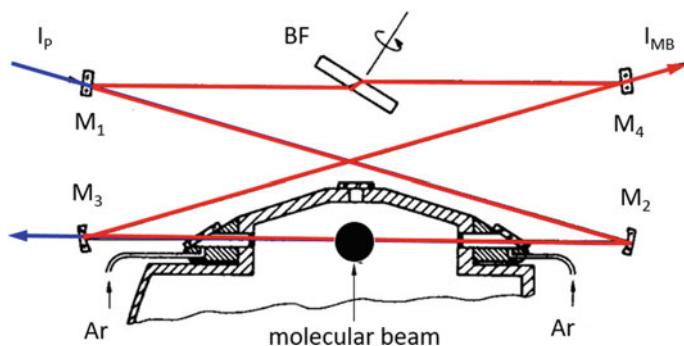


Fig. 8 The optical laser cavity built around the molecular beam in a vacuum chamber. I_p is the pump laser and I_{MB} the molecular-beam laser radiation. Only a small fraction of the pump laser is absorbed in the beam. Therefore, the pump laser exits again through the mirror M_3 . BF is the birefringent (a tunable optical) filter that controls to which vibrational level v'' in the electronic ground state lasing is possible

and the molecular beam was operating. Upon turning on the pump laser lasing was immediately observed. The laser operated for about 15 min and then it went off. It took us 6 months (!) to get it back into operation. This task was accomplished by Uli Gaubatz, who had joined the group shortly after the first operation of the laser was observed. Without these crucial 15 min, proving that the concept works, we would have probably given up after a few months and, most likely, the successful path towards realizing STIRAP would have been abandoned.

It turned out that one of the problems was the alkali deposit on the intra-cavity windows (see Figs. 8 and 9), separating the vacuum region from the outside. After several trial-and-error modifications, the problems were overcome. One of the measures was the heating of the windows to high temperatures what required the use of metal rings for vacuum-tight sealing. Furthermore, the installation of small pipes that directed a flow of Argon atoms away from the windows reduced the rate of deposit of alkali atoms and molecules on the windows. With these measures the molecular-beam laser could be routinely operated and in 1986 we set out to determine the properties of the transfer process, in particular its efficiency and selectivity [26].

The delay of a couple of years between the first demonstration of successful laser operation and the attempt to use such a laser for quantitative population transfer was in part due to the fact that no apparatus was available for such experiments. Students needed to first complete their ongoing experiments. The time was used to further explore the physics of the molecular-beam laser [27, 28]. Later we also built a molecular-beam laser with iodine molecules using a slit-nozzle expansion. For the latter system an optical pump-power threshold for starting the laser operation as low as 250 nW [29] was demonstrated.



Fig. 9 View through a window into the gain region of the molecular beam laser. The glowing red part is the molecular beam source with a cooler (darker) thermocouple attached. The thin yellow trace marks the pump laser beam which excites also background molecules. The thicker yellow region is seen because of radiation diffusion between particles along streamlines of the molecular beam. The gain region is the crossing between the two yellow traces

5 The Breakthrough

Figure 10 explains how the molecular-beam laser induced transfer efficiency was

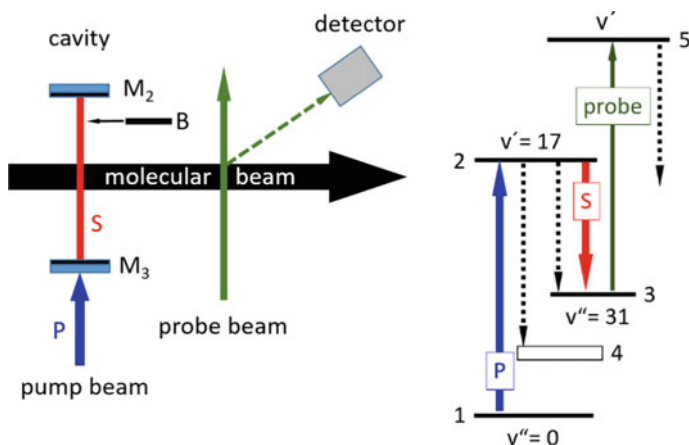


Fig. 10 Schematic of the set up (left part) for the calibration of the transfer efficiency induced by the molecular beam laser from level 1 ($v'' = 0$) to level 3 ($v'' = 31$). The element B is used to block the cavity. The related level scheme is shown in the right. Levels other than 1 and 3 that can also be reached from level 2 by spontaneous emission are summarized as level 4. The transfer into level 3 is probed by laser-induced fluorescence from level 5

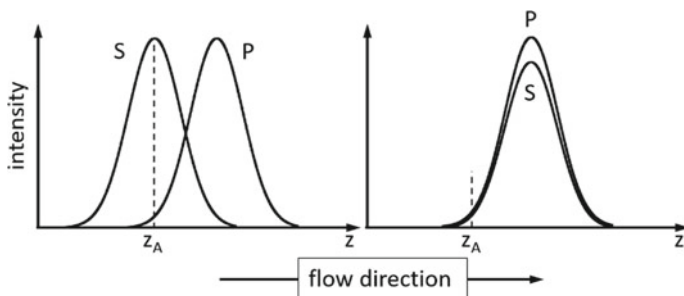


Fig. 11 The right part shows the P- and S- laser with coincident axes, as realized in the molecular-beam laser arrangement of Fig. 8. The left part shows the S-before-P arrangement of the lasers as also seen in the lower part of Fig. 1. The position z_A marks the location near which the pump laser would start pumping molecules out of level 1

determined. The pump laser excited molecules from the level $v'' = 0$ to $v' = 17$ in the B-state of Na_2 , followed by spontaneous emission. The population in the target level of interest, e.g. $v'' = 31$, was probed by laser-induced fluorescence further downstream with the cavity blocked. Because the optical transition probabilities are known and after confirming that the population in level 1 was entirely depleted, the transfer efficiency of the population reaching level $v'' = 31$ by spontaneous emission could be determined. Unblocking the cavity allowed the molecular-beam laser to operate and the population in the target level increased. The increase of the population in relation to the known transfer efficiency by spontaneous emission yielded the beam-laser induced transfer efficiency. It was found [26] that the transfer efficiency was as large as 75% (larger than any other scheme would allow) but it was still far from the goal of $\approx 100\%$. The question thus was: what limits the transfer efficiency to about 75%?

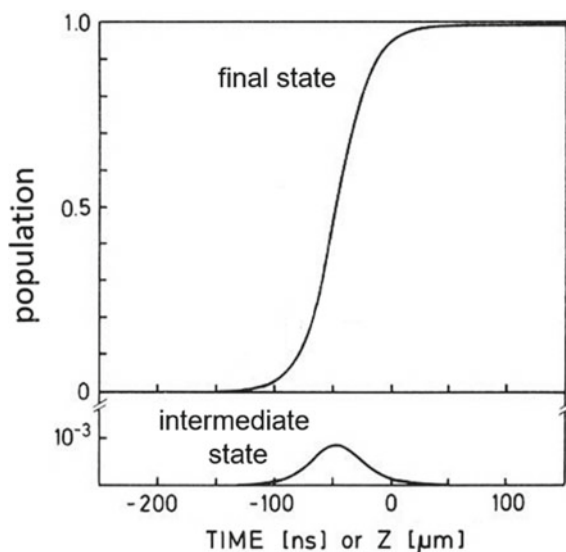
The solution, which paved the final segment on the path to STIRAP, was surprisingly simple, as shown in Fig. 11. Results from earlier work on the consequences of optical pumping in two-step photoionization [30] led the way. The right part of Fig. 11 shows the profiles of the pump laser and the molecular-beam laser which appears after the pump laser is switched on. The axes of the two laser fields coincide. The molecules travel from left to right. As soon as the molecules reach the wings of the pump laser profile (P) they are efficiently pumped to the upper laser level. At the location z_A , however, the local molecular-beam laser intensity, which is supported by molecules that had already crossed the cavity, is still weak. Therefore, stimulated emission induced by the radiation field S that is supposed to populate level 3 (the target level) cannot yet compete with spontaneous emission. In fact, the transit time of the molecules across the cavity is about one order of magnitude longer than the radiative lifetime in level 2, the upper laser level. Therefore, only a fraction of the relevant molecules reaches the axis of the cavity where the beam laser is sufficiently strong to allow stimulated emission to compete successfully with spontaneous processes.

The final conclusion was again straightforward. Despite the significant effort invested to realize it, the molecular-beam laser approach had to be abandoned. In addition to the pump laser, an external laser for driving the stimulated emission process was needed, with its axis placed upstream of the axis of the pump laser, as shown in the left part of Fig. 11. As soon as the molecules enter the wings of the pump laser profile, they should be exposed to the maximum possible intensity of the S-Laser to optimize the chance for successful competition of stimulated emission with spontaneous processes. The informed reader realizes that the above argument, with optical pumping processes in mind, doesn't yet properly catch an essential part of STIRAP physics. It provided, however, the rationale for placing the axis of the S-beam upstream of the one for the P-beam, with a suitable overlap between the two.

It was very fortunate that Piotr Rudecki, a visiting scientist from Torun/Poland, arrived in the fall of 1987 a few days after I had come to the conclusion that a S-before-P arrangement was needed. The experiment which he wanted to join was not ready yet. However, he had some experience in modeling radiative processes. Therefore, I asked him to take our code for simulating the molecular-beam laser, which we had developed with the help of Wellegehausen, and modify it in accordance with the new geometry. The hope was to quantitatively understand the benefit of the S-before-P configuration from results of simulation studies. I certainly did expect a transfer efficiency of more than 75%.

About 10 days later, Rudecki presented his results: nearly 100% transfer. Expecting something near 90%, my reaction was: "hard to believe, please check for errors". A few days later, Piotr joined the group for the traditional after-lunch coffee-and-discussion meeting at a round table near the lab, presented the results of new calculations (see Fig. 12) and stated firmly "no errors—100% is correct". I

Fig. 12 The first numerical results for the transfer of the population of level 1 to level 3 (the final level) with a laser arrangement as shown in the lower part of Fig. 1. The lower part shows the transient population in the intermediate level 2. While, at late times, the final state population approaches unity, the maximal transient population of the intermediate level is 10^{-3}



clearly recall my prompt reaction: “congratulation—this result will be a big bang in the community and will determine what we do in the lab for the next 10 years”.

A few months later, in early 1988, we managed to demonstrate that a very high population transfer can indeed be realized in the S-before-P configuration. In a first short publication [31], we showed results, but the theoretical basis had not yet been clearly sorted out. This gap was closed by the May 1, 1990 publication in *J. Chem. Phys.* [1], with Uli Gaubatz being the leading graduate student who had noted the close connection of what we did with the work by Claude Cohen-Tannoudji [32]. Prior to submitting the manuscript of paper [1], a detailed discussion of the adiabatic condition was published [2]. The paper [1] remains a standard reference for STIRAP and indeed, all the basic features that make STIRAP unique are experimentally documented and theoretically properly analyzed in that work. In that paper, also the acronym STIRAP was introduced. Regarding the latter, I had learned earlier that it is important to give a name to a new technique, method or process before others will do it. After the first rough draft of the paper was ready, I told my students that instead of joining the after-lunch meeting, I will spend one hour or two in my home-office and come back with a suggestion for an acronym. At home, I wrote down all physical processes or phenomena that had some connection to the transfer process, looked at the initial letter or letters and wrote them down in different orders. The criteria were: the acronym should have no more than two syllables and pronunciation should be easy. I returned to the lab with the suggestion STIRAP, which was accepted by all involved.

We defined the publication date or ref [1], May 1st, 1990 the “birthday” of STIRAP and celebrated its 25th anniversary in September 2015 with a well-attended and well-received international conference in Kaiserslautern [33].

6 Some STIRAP Highlights that Followed

The most recent compilation of some highlights regarding STIRAP applications can be found under [7]. Here a few topics are listed, with only one or two references given:

- preparation of ultracold molecules, see e.g. [34, 35]
- reduction of the upper limit of the electric dipole moment of the electron [36]
- controlling the phase of superposition states [37, 38]
- new tools for matter wave optics [39, 40]
- population transfer in superconducting circuits with relevance to quantum information [41, 42]
- single photon generation by sending atoms through an optical cavity [43]
- control of the pathway of light in optical fiber networks [44]
- population transfer in a solid-state environment [45, 46]
- controlled modification of the quantum state in strings of ions bound in a trap [47]

- use of the concept for acoustic waves with the potential to improve hearing aids [48]
- control of the flow of spin-waves in a network of suitable wave-guides [49]

The application of the STIRAP-approach to acoustic waves [48] is a particularly nice example for how far reaching the concept is. It also underlines that STIRAP is not a purely quantum mechanical process.

There are also a number of proposals with a detailed analysis of the feasibility of STIRAP applications, such as

- implementing quantum gates, e.g. [50–52]
- cooling particles in an atomic beam [53]
- excitation of molecular Rydberg states, by-passing predissociation levels [54]
- preparation of highly polarized molecular quantum states [55]
- storage of energy using nuclear isomers [56]
- spatial adiabatic passage (SAP, transfer of particles between traps) [57]
- digital pulse sequences, optimized via a learning algorithm, to speed up the process [58]

The example (SAP, in earlier years also called CTAP—coherent transport by adiabatic passage) would be a particularly intriguing demonstration of the STIRAP-concept: Consider three traps A, B and C in a linear arrangement and close proximity. Each trap is able to hold a single particle. Assume that one particle is initially in trap A while B and C are empty. When the coupling between the traps is properly varied as required for STIRAP (e.g. by lowering the barriers between them while keeping the quantum states in the traps in resonance) the particle is removed from A and appears in C without establishing a significant transient population in B.

7 Final Remarks

Following the original publication in 1990, the STIRAP concept has been systematically developed, both experimentally and theoretically, in Kaiserslautern (with too many publications to be all listed), also for applications beyond the canonical three-level system. That work benefitted greatly from the contributions of the visiting scientists Bruce W. Shore, Leonid P. Yatsenko, Razmik Unanyan, Matthew Fewell, and Nikolay V. Vitanov. Experimental progress was achieved through the dedicated work of many excellent students: Axel Kuhn, Stefan Schieman, Jürgen Martin, Thomas Halfmann, Heiko Theuer, and Frank Vewinger to name at least some. The post-docs George Coulston, Horst-Günter Rubahn, and Stéphane Guérin also contributed significantly to the successful developments.

At the occasion of my first public presentation of the concept in the colloquium at JILA/Boulder on March 1st, 1990 (i.e. prior to the publication of [1]) I had the chance to discuss STIRAP with Peter Zoller. It was the follow-up theoretical and

experimental work from the groups of Peter Zoller and Bill Phillips [59, 60], respectively, on matter-wave mirrors and beam splitters and the experimental work in the group of Steve Chu on atom interferometry [39], that made STIRAP quickly known in the AMO community. Nevertheless, it took more than 10 years after the original publication [1] before STIRAP was used in many laboratories and in different areas of research.

Several proposals did appear in the literature discussing the prospects for applying STIRAP to poly-atomic molecules. However, nearly all of them are based on model systems that did not adequately include relevant properties, such as the realistically modelled (detrimental) high level density. The consequences of the inclusion of these properties are carefully analyzed in an extensive simulation study [61] involving the HCN molecule. To the best of my knowledge, SO₂ is still the largest, or most complex, molecule to which STIRAP has been successfully applied [62] in an experiment.

As explained in Sect. 3, the STIRAP-concept was developed with reaction dynamics experiments involving vibrationally excited molecules in mind. One early experiment of that kind has been completed in Kaiserslautern (Na₂(v'') + Cl → NaCl + Na* [63]). Using STIRAP was also essential in the recent observation of bimolecular reactions at ultracold temperatures [64]. However, the initial motivation had reactions of relevance to atmospheric chemistry in mind. Such an application still awaits its realization. Because of recent developments of coherent radiation sources for the region $\lambda < 200$ nm, this situation may change soon. The related requirements for the molecules H₂, N₂, O₂, and OH are discussed in the appendix of [5].

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