

Perspective: Stimulated Raman adiabatic passage: The status after 25 years

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The first presentation of the STIRAP (stimulated Raman adiabatic passage) technique with proper theoretical foundation and convincing experimental data appeared 25 years ago, in the May 1st, 1990 issue of The Journal of Chemical Physics. By now, the STIRAP concept has been successfully applied in many different fields of physics, chemistry, and beyond. In this article, we comment briefly on the initial motivation of the work, namely, the study of reaction dynamics of vibrationally excited small molecules, and how this initial idea led to the documented success. We proceed by providing a brief discussion of the physics of STIRAP and how the method was developed over the years, before discussing a few examples from the amazingly wide range of applications which STIRAP now enjoys, with the aim to stimulate further use of the concept. Finally, we mention some promising future directions. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4916903>]

I. THE DISCOVERY OF STIMULATED RAMAN ADIABATIC PASSAGE (STIRAP)

This article appears in print in J. Chem. Phys. exactly 25 years after publication of the original paper¹ that presented STIRAP as a new method for almost lossless population transfer between quantum states. We here describe the history behind the development of STIRAP including the main initial motivation for the work (Sec. I) and its basic theory (Sec. II). We also discuss crucial steps in the development of the technique, emphasizing key results—what works well and what does not (Sec. III). We also highlight some of the more recent applications (Sec. IV) and offer suggestions about what new and possibly important experiments STIRAP could make possible in the near future (Sec. V). We do not aim at complete coverage of the relevant literature; only selected work is referenced.

A. Setting the goal

In the late 1970s, results were reported^{2,3} from experiments that used, for the first time, laser methods for state selection in studies of molecular-collision dynamics in crossed-particle beams. Those experiments used laser-induced fluorescence to monitor the angular distribution of molecules scattered into the rotational level j_f'' of the vibrational ground state. They provided data of unprecedented detail on the dynamics of molecular collision processes. In that work, the thermal population of a specific rotational level j_i'' in the vibrational ground state $v_i'' = 0$ of the incoming molecules was depleted, prior to reaching the scattering center, through optical pumping by a laser field P . With P present, the thermal population of the given level was excited and then transferred by spontaneous emission to higher lying vibrational levels. Rotational levels

of $v'' = 0$ that received population by collisions did not get populated by fluorescence, and collisional transfer from $v'' > 0$ into $v'' = 0$ was negligible. Thus, from the angular distribution of the difference between the scattering signals with the P laser on and off, the experimenters obtained the relative state-to-state differential cross section for the rotationally inelastic process ($j_i'' \rightarrow j_f''$). The data showed fine details of the collision dynamics.⁴

The success of the experiments referenced above motivated plans for work with vibrationally highly excited molecules. It seemed of particular interest to understand details of how vibrational excitation controls energy transfer and reactions, because such reactions play a significant role in many molecular reactions and environments, e.g., atmospheric chemistry. However, in order to proceed, it was necessary to find a method that would efficiently and selectively transfer population from a thermally populated level to one and only one high-lying vibrational level. Selectivity is important because the addition of the energy of one vibrational quantum may alter the reaction dynamics dramatically. A method suitable for the set task needed to satisfy a number of essential requirements, such as

- efficiency and selectivity*: the population of a given level needs to be transferred (almost entirely) to a specified single higher lying level;
- robustness*: the efficiency of the transfer must be insensitive to small variations of the optical transition rate including insensitivity to small variations of the parameters of the radiation fields and the optical properties of the particle;
- flexibility*: within certain limits (e.g., those imposed by Franck-Condon factors), one should be able to freely choose the target level.



Requirement (a) has already been justified. Requirement (b) is needed for two reasons: first, it must be possible to induce the transfer across a substantial fraction of the molecular beam in order to have a sufficiently high flux for the scattering experiment. Second, it is often desirable to transfer the entire population of a rotational level, independent of the orientation of the angular momentum, i.e., independent of the magnetic sublevel. Requirement (c) is inherent in the set task, namely, the study of the variation of the collision dynamics as the vibrational level is changed.

None of the optical methods known at that time (around 1980) for altering the population distribution within a quantum structure met all three requirements. For example, transfer by electronic excitation followed by spontaneous emission (Franck-Condon pumping, FCP) obviously lacks selectivity. Transfer by stimulated Raman scattering (SRS⁵) lacks flexibility, because it is limited to excitation of the first vibrational level or, if high laser power is available, the first few vibrational levels. Transfer by two consecutive pi-pulses (or a two-photon pi-pulse) lacks robustness, because it requires precise control of the temporal pulse area (proportional to the optical transition moment and laser field amplitude) integrated over the particle-laser interaction time. Also the very successful method of stimulated emission pumping (SEP), developed in the early 1980s^{6,7} and later used in many collision dynamics studies,^{8,9} does not come close to meeting all the three requirements. The transfer efficiency of SEP is limited to the order of 30% (although 10% is typical) and it places population into levels other than the target level. (A method to reduce the population in these other levels has recently been demonstrated.¹⁰) Therefore, it was concluded, and stated by Bergmann,¹¹ that a new approach was needed and the goal was set to find one.

B. A promising attempt

Inspiration for a new approach to achieving the goal came from the work on optically pumped dimer lasers¹² using the molecules of alkali vapor in a heat pipe as the gain medium. In that work, a specific vibrational level v' in a suitable electronic state was populated by a laser P . Since population inversion to thermally unpopulated high-lying vibrational levels v'' in the electronic ground state is easily established, lasing is possible. A cavity-internal optical filter may restrict lasing to a specific level v'' , thereby transferring population predominantly to that level. Continuous lasing is possible if relaxation processes remove the population of level v'' sufficiently rapidly. It was demonstrated that such lasers can be operated with rather low threshold pump power; the record low for the heat-pipe work was 0.5 mW.¹²

A “back of the envelope” calculation showed that the total number of molecules which are available for possible laser action in the collision-free region close to the nozzle of a supersonic molecular beam would be higher than in a heat pipe. This is true, despite the much smaller length of the interaction zone between laser beam and particles (on the order of 1 mm) compared with a heat pipe (on the order of 100 mm), because the beam has a much lower temperature for the internal degrees of freedom. Thus, although the total number of molecules is

smaller in the particle beam, there are more in a low-lying rotational level of the vibrational ground-level.

Therefore, a very promising route to achieve the goal seemed to be to build a laser cavity around the supersonic beam, optically pump the molecules into a suitably chosen level in an electronic state as they travel across the axis of the cavity, and insert an optical filter element that would restrict laser action to transitions between the electronically excited state and the targeted high-lying vibrational level of the electronic ground state. The hope was that the combination of efficient excitation into the electronic state together with the selectivity of the laser action would fulfill the task and provide selective, efficient, robust, and flexible population transfer. Indeed, the concept for an optically pumped laser with molecules in a supersonic beam being the active medium was shown to work well with a beam of sodium dimers¹³ and a threshold pump power as low as 250 nW was achieved for an iodine-beam laser.¹⁴

The picture used at that time was based on rate equations. That picture appeared justified, since some molecules would cross the laser beams near their axis, others along the wings. Thus, any Rabi cycling would wash out when averaged over that part of the cross section of the molecular beam which is exposed to the radiation fields.

The viewpoint at the time was the following. We consider a thermally populated rotational level j'' in the electronic and vibrational ground state, $v_1'' = 0$ (level 1). (We do not keep track of the rotational quantum numbers of the levels because they are determined by optical selection rules.)

We also consider the volume V given by the overlap of the laser P and the molecular beam. The molecular flow continuously feeds fresh molecules into level 1 in the given volume. These molecules are excited by the laser P with a suitably chosen wavelength to vibrational level v' in an electronic state (level 2, the upper laser level). From level 2, molecules undergo the transition to a selected sufficiently high lying vibrational level v_3'' of the electronic ground state (level 3, the target state). Selection occurs by a suitable optical filter within the cavity. These transitions are stimulated by the radiation field S in the cavity that has been established by prior emission processes. The molecular flow carries the molecules out of the considered volume and away from the two radiation fields. (Without the molecular flow or without collisional relaxation, the initial population in level 1 would quickly be equally shared by all three levels; inversion—and thus lasing—could not be maintained.)

The question was how much of the initial population of level 1 entering the upstream side of V would reach level 3 at the downstream side of V and then be carried away by the molecular flow, available to do, e.g., scattering experiments. Detailed experimental studies¹⁵ revealed that this concept produces a transfer efficiency substantially above 50%, i.e., significantly higher than with any other method demonstrated at that time. This is because the molecules, excited to an electronic state by the P laser, are efficiently stimulated down to the target level by the generated laser-beam S . In so doing, they provide photons for the S field. The demonstrated efficiency¹⁵ of 70% was, however, still disappointingly far away from the set goal of “nearly 100%.”

C. Reaching the goal

The goal was reached after implementing changes which were motivated by the following consideration, based again on a rate-equation picture. The laser beam S , generated by optical pumping as explained above, is necessarily confined to the axis of the cavity, and thus, the driving laser-field P must also propagate along that axis. New molecules traveling towards the cavity to further feed the laser action find themselves first in the wings of these two lasers, P and S . The P laser is already strong enough to excite molecules in level 1 to the upper laser level (level 2) but the S laser is not yet strong enough for the rate of stimulated emission to the target level to compete successfully with the rate of spontaneous emission. Thus, before reaching the center of the cavity, many molecules are lost by spontaneous emission to levels other than the target level, thereby spoiling efficiency and selectivity.

After model calculations had confirmed the validity of that view, a remedy was quickly found: remove the cavity and bring in a second external laser S , with its center shifted upstream of the axis of laser P . The molecules would then be interacting with a strong S field as they reached the wings of the P laser. Therefore, the rate of stimulated emission, induced by the S field, would be sufficiently large to compete with spontaneous emission as soon as molecules have traveled far enough to be excited by the P laser.

Modification of the molecular-beam-laser modeling code (using a density-matrix approach)¹⁵ to include the spatial shift of the two laser fields (a timing offset between the two fields affecting the molecules) confirmed that (nearly) 100% transfer efficiency should be achievable. This prediction was in fact experimentally demonstrated soon afterwards,¹⁶ where it was noted that “the proposed and demonstrated technique does not

require laser intensity modulation, laser frequency chirping, or level shifting.”

The mechanism for producing the nearly complete population transfer, as it is understood today, is actually rooted deeper in interesting physics than was initially anticipated. It involves coherent adiabatic evolution of a dark, population-trapping state as molecules pass through slowly varying fields, first S and then P . The full theory, and the acronym STIRAP, was finally presented in a J. Chem. Phys. paper¹ together with a convincing set of experimental data.

II. THE PHYSICS OF STIRAP IN A NUTSHELL

A. The STIRAP equations

The physics of STIRAP, well understood by now, and its applications have been reviewed in several articles.^{17–23} The STIRAP process involves coherent excitation in a three-state chain, 1–2–3 induced by two pulsed fields, P with carrier frequency ω_P linking states 1 and 2 and S with carrier frequency ω_S linking states 2 and 3.

Figure 1(b) shows an example of the lambda linkage pattern of Hamiltonian interactions that are involved in STIRAP. (Ladder linkages, defined by energy rankings $E_1 < E_2 < E_3$, are also possible.^{19,20,23}) This shows the P -field linkage between two states and the S -field linkage that selects a single target state from a set of states with similar energies. Frame (c) shows a schematic linkage in which the intermediate excited state is from a continuum, as discussed in Sec. III E. Frame (a) shows, schematically, the time ordering of the S and P pulses, here depicted as having equal widths and heights.

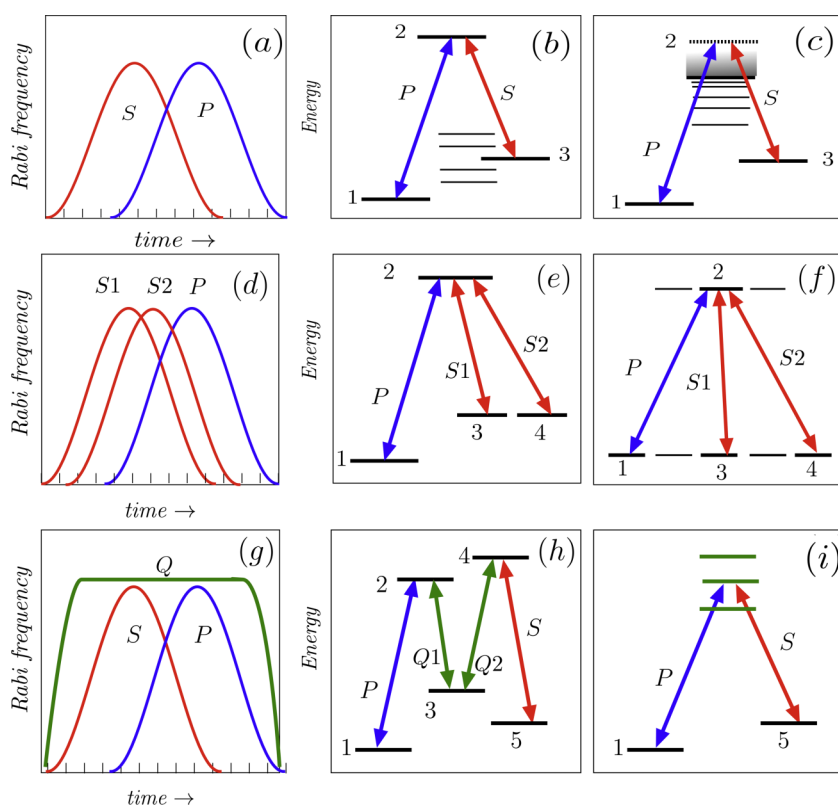


FIG. 1. Pulse sequences and linkages. (a) Schematic of timing for S and P Rabi-frequency-pulses of STIRAP. (b) Lambda linkage pattern for traditional STIRAP. State 1 is initially populated. Two-photon resonance conditions have selected target state 3 from neighboring alternatives. (c) Continuum STIRAP, with linkage through a continuum of intermediate states, see Sec. III E. (d) Pulse sequence for tripod linkage and fields P, S_1, S_2 . (e) Four-state tripod linkage with fields P, S_1, S_2 . (f) Linkage pattern as found in linkage of degenerate Zeeman-sublevels. Laser polarization choice determines the linkages. (g) Schematic of pulse sequence for straddle-STIRAP: overlapping the traditional S and P pulses is a pulse or pulses Q that connect intermediate states. (h) The five-state letter-M linkage for straddle-STIRAP, cf. Sec. III G. (i) Equivalent linkage pattern involving, as intermediate states, adiabatic states formed from bare states 2,3,4 by the straddling interactions Q .

In the traditional laser-induced STIRAP, the interaction Hamiltonian is that of an atomic or molecular dipole-transition moment \mathbf{d} in the electric field of a laser, evaluated at the center of mass,

$$\mathbf{E}(t) = \text{Re} \left[\mathbf{e}_P \mathcal{E}_P(t) \exp(-i\omega_P t + i\varphi_P) + \mathbf{e}_S \mathcal{E}_S(t) \exp(-i\omega_S t + i\varphi_S) \right], \quad (1)$$

where \mathbf{e}_P and \mathbf{e}_S are unit vectors, $\mathcal{E}_P(t)$ and $\mathcal{E}_S(t)$ are slowly varying pulse envelopes, and φ_P and φ_S are constant phases.

The dynamics of this process is governed by a set of coupled ordinary differential equations for probability amplitudes $C_n(t)$ for the three states, as implementation of the time-dependent Schrödinger equation,

$$i \frac{d}{dt} \mathbf{C}(t) = \mathbf{W}(t) \mathbf{C}(t). \quad (2)$$

Here, $\mathbf{C}(t)$ is a column vector of 3 probability amplitudes and, with appropriate definitions of the time-varying phases of these amplitudes,^{22,23} $\mathbf{W}(t)$ is a 3×3 matrix obtained from the original Hamiltonian by making the rotating-wave approximation (RWA) and having at least two null diagonal elements,

$$\mathbf{W}(t) \mathbf{C}(t) \equiv \frac{1}{2} \begin{bmatrix} 0 & \Omega_P(t) & 0 \\ \Omega_P(t) & 2\Delta & \Omega_S(t) \\ 0 & \Omega_S(t) & 0 \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \\ C_3(t) \end{bmatrix}. \quad (3)$$

The zero in the upper-left corner originates with the choice of state 1 as the zero of energy; with this choice, the zero of the lower-right corner expresses the two-photon resonance condition. The off-diagonal elements of the RWA Hamiltonian matrix $\mathbf{W}(t)$ are parametrized by slowly varying Rabi frequencies $\Omega_P(t)$ and $\Omega_S(t)$, projections of dipole moments onto the electric fields and assumed to be real-valued,

$$\hbar\Omega_P(t) = -\mathbf{d}_{12} \cdot \mathbf{e}_P \mathcal{E}_P(t), \quad (4a)$$

$$\hbar\Omega_S(t) = -\mathbf{d}_{23} \cdot \mathbf{e}_S \mathcal{E}_S(t). \quad (4b)$$

The constant nonzero diagonal element Δ is the detuning. For the usual lambda linkage, in which the undisturbed energies are ordered $E_2 > E_1, E_3$, it is evaluated from the formulas

$$\hbar\Delta = E_2 - E_1 - \hbar\omega_P = E_2 - E_3 - \hbar\omega_S. \quad (5)$$

Equation (3) for $\mathbf{W}(t)$ and the STIRAP process combine to require that the two carrier frequencies satisfy the two-photon resonance condition,

$$E_3 - E_1 = \hbar(\omega_P - \omega_S). \quad (6)$$

Note that Eq. (3) makes no reference to the original energies E_n , only to their relationship to carrier frequencies through detunings. Thus, the ordering of these energies is irrelevant for STIRAP: the “ladder” linkage is, in principle, as usable as the lambda linkage although the final state will have spontaneous-emission loss.

B. Adiabatic eigenvectors

As was first pointed out by Kuklinski *et al.*,²⁴ the mathematical description of STIRAP is facilitated by introducing

instantaneous eigenvectors of the slowly varying RWA Hamiltonian matrix $\mathbf{W}(t)$ (corresponding to adiabatic states),

$$\mathbf{W}(t) |a^\mu\rangle = \varepsilon_\mu(t) |a^\mu\rangle. \quad (7)$$

For three-state systems, as with STIRAP, the usual labels are $\mu = -, 0, +$. When the changes of $\mathbf{W}(t)$ are sufficiently slow (adiabatic), then the statevector will remain fixed in the coordinate system of adiabatic states. One of these,

$$|a^0\rangle = \frac{1}{\Omega_{\text{rms}}(t)} \begin{bmatrix} \Omega_S(t) \\ 0 \\ -\Omega_P(t) \end{bmatrix}, \quad (8)$$

where

$$\Omega_{\text{rms}}(t) = \sqrt{\Omega_P(t)^2 + \Omega_S(t)^2} \quad (9)$$

has no population in excited state 2 from which spontaneous emission could occur: its coherent superposition is associated with a “dark state” (or “population trapping” state).²⁵ [With the phase choice that produces the $\mathbf{W}(t)$ of Eq. (3), this vector has constant null eigenvalue, $\varepsilon_0(t) = 0$, but other choices have been used.²³] By controlling the relative magnitude of the two Rabi frequencies, an experimenter controls the relative portion of the two constituents of the dark state, traditionally parametrized by the mixing angle $\theta(t)$,

$$\tan \theta(t) = \Omega_P(t)/\Omega_S(t). \quad (10)$$

That is, the dark adiabatic state has the construction

$$|a^0\rangle = \begin{bmatrix} \cos \theta(t) \\ 0 \\ -\sin \theta(t) \end{bmatrix}. \quad (11)$$

When the S field is much stronger than the P field, this eigenvector is aligned with initially populated state 1. It becomes aligned with target state 3 when the P field is much stronger than the S field. If the change of the mixing angle is slow (adiabatic change), the statevector will remain aligned with (“adiabatically follow”) $|a^0\rangle$. Thus, by inducing a sweep of the mixing angle from 0 (dominant S field) to $\pi/2$ (dominant P field), and maintaining alignment between the statevector and $|a^0\rangle$, an experimenter can transfer populations from state 1 to state 3 via the dark state without ever placing population in middle state 2: this is STIRAP.

C. The STIRAP pulse sequence

The pulsed fields required by STIRAP can arise in two ways. In the original work, a beam of molecules passed through two cw laser beams whose parallel axes were slightly offset. The spatial variation of the electric field across the laser-beam profiles (Gaussians) translated into a time dependence. A second approach used pulsed laser fields having smooth envelopes.

The required pulse sequence for STIRAP, shown in frame (a) of Fig. 2, is that the S pulse precedes but overlaps the P pulse, an ordering known as “counterintuitive” because the first action, by the S pulse, is between two unpopulated states; the “intuitive” ordering, P before S , would move population into intermediate state 2, from where spontaneous emission may

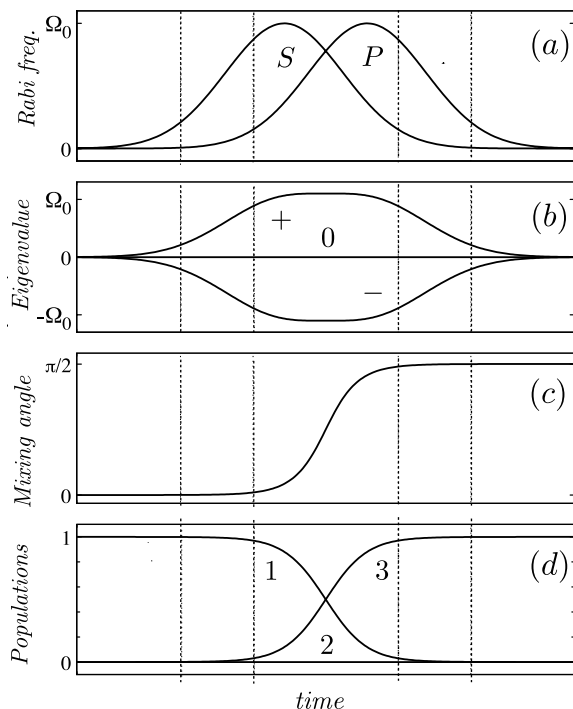


FIG. 2. The time dependence of various quantities associated with STIRAP for Gaussian pulses optimally delayed: (a) the P and S Rabi frequencies, (b) the adiabatic eigenvalues ε , (c) the mixing angle θ , (d) the populations P_n . The dotted lines separate characteristically different circumstances (from left to right): (1) S laser weak, no P laser present; (2) S laser strong, P laser weak; (3) both S and P lasers strong; (4) S laser weak, P laser strong; (5) no S laser, P laser weak. Adapted with permission from Fig. 8 of Vitanov *et al.* Adv. At., Mol., Opt. Phys. **46**, 57–190 (2001). Copyright 2001 by Academic Press.

populate other levels and would lead to Rabi oscillations of the population between the coupled states. With STIRAP, state 2 remains unpopulated when the statevector is aligned with the dark adiabatic state.

The S -first pulse ordering is a defining characteristic of STIRAP, as is the lack of population in state 2. Figure 3 illustrates this timing requirement, for experiments in which an atomic beam of metastable neon atoms pass through parallel cw laser beams, each tuned to resonance with respective transitions (so that $\Delta = 0$). The spatial offset of the beams produces a time delay of two Gaussian pulses.¹ Maximum excitation occurs when the peak of the S pulse precedes that of the P pulse by about a laser-beam width.

D. The adiabaticity criteria

The conditions for adiabatic evolution in STIRAP have been expressed in various ways.^{1,19,23} Basically, these come from the requirement that change of the RWA Hamiltonian $W(t)$ be very slow. For the STIRAP system, this becomes the requirement that the rate of change in the mixing angle, $\dot{\theta}(t)$, be much less than the eigenvalue separation, which for fully resonant excitation ($\Delta = 0$) is the rms Rabi frequency

$$|\dot{\theta}(t)| \ll \Omega_{\text{rms}}(t). \quad (12)$$

This is a “local condition” for adiabatic evolution, and it must be satisfied at all times. The pulses must therefore be smooth, with no rapid variations of the field amplitude.

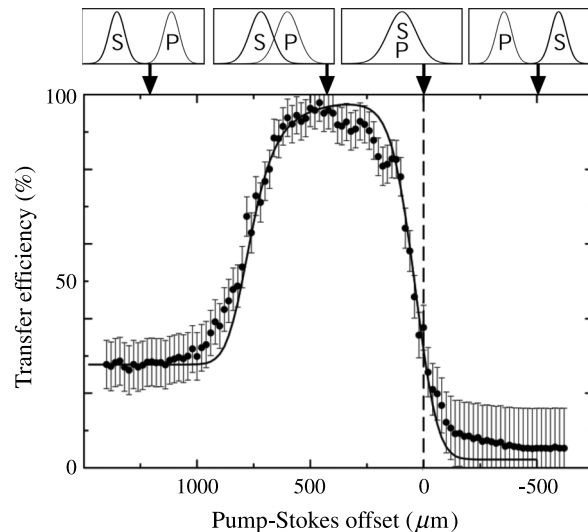


FIG. 3. Population transfer in metastable neon as a function of the spatial offset of the P and S beams. Insets along the top show the relative positions of the S and P pulses. Positive offset means P before S . Reprinted with permission from Fig. 9 of Bergmann *et al.* Rev. Mod. Phys. **70**, 1003–1023 (1998). Copyright 1998 by APS.

The early papers on STIRAP,^{1,24} wishing to express this inequality with more global properties, dealt with Gaussian pulses of equal peak Rabi frequency and Gaussian width T , for which each Rabi frequency had time dependence of the form $\Omega(t) = \Omega_{\text{max}} e^{-(t/T)^2}$. They found, for optimally delayed Gaussian pulses having equal peak value, the requirement that the product $\Omega_{\text{max}} T$ be large. As noted by Vitanov *et al.*,¹⁹ experience suggests the adiabatic criterion

$$\Omega_{\text{max}} T \geq 10 \quad \text{or} \quad \Omega_{\text{max}} \geq \frac{10}{T} \quad (13)$$

for each pulse. This criterion can be expressed in other ways.

- Because the Fourier transform of the Gaussian $e^{-(t/T)^2}$ is proportional to the Gaussian $e^{-(\omega T)^2}$, the transform-limited spectral bandwidth is $\Delta\omega = 1/T$ and we may also read Eq. (13) as stating that the peak Rabi frequency should be about 10 times larger than the transform-limited bandwidth.
- The product $\Omega_{\text{max}} T$ is, apart from a pulse-shape dependent factor of the order of unity¹⁹ (equal to $\sqrt{\pi}$ for a Gaussian), the temporal pulse area (time-integrated Rabi frequency) in radians. Thus, for a Gaussian pulse, adiabaticity criteria (13) can also be expressed as the requirement that the pulse area be larger than around 6π , a value noted in Ref. 23 as leading to 99% population transfer. For a resonant two-state transition,^{22,23,26} a pulse having this temporal area would produce 3 full Rabi cycles of population oscillation.^{22,26}

E. Detunings

Although complete population transfer can occur with nonzero detuning Δ , it is most efficient (i.e., requires least laser power) when each laser frequency is resonant, so that $\Delta = 0$. However, successful population transfer can also take place

adiabatically when two-photon resonance condition (6) is not satisfied.

With nonzero two-photon detuning, each of the adiabatic eigenvectors acquires a component of state 2 and thereby acquires potential loss through spontaneous emission. The connection between the initial state and the target state is by means of a “transfer state,”²⁷ an adiabatic eigenvector which is not necessarily a dark state, a condition required for STIRAP.²³

An alternative technique for three-state adiabatic passage sweeps the detuning through the two-photon resonance, as proposed by Oreg *et al.*²⁸ This procedure, chirped rapid adiabatic passage (CHIRAP) or Raman chirped adiabatic passage (RCAP), see Ref. 23, can be accomplished in several ways. (As explained elsewhere,²³ this is not STIRAP.) The frequency of one laser can be swept (chirped) while maintaining a fixed frequency difference (in case of a lambda linkage) or sum frequency (in case of a ladder linking).²⁹ The needed sweep of two-photon detuning can also be accomplished when excitation involves only a single laser, one that is used in a ladder linkage 1-2-3 in which the energy spacing between states 2 and 3 is nearly equal to that between states 1 and 2, and the sweeping laser frequency first becomes resonant with the 2-3 transition and then with the 1-2 transition.^{28,30,31}

F. Ensemble averages

Any time-dependent Schrödinger equation applies to individual quantum systems, e.g., single isolated atoms or molecules. Experiments generally deal with ensembles of individual systems, each distinguished by some attribute e such as center-of-mass motion, initial orientation (Zeeman sublevel M), initial excitation energy, or arrangement of neighboring particles. Each individual system obeys an equation of the form

$$i \frac{d}{dt} \mathbf{C}(e; t) = \mathbf{W}(e; t) \mathbf{C}(e; t). \quad (14)$$

What is experimentally observable is the ensemble average

$$P_n(t) = \sum_e p(e) |C_n(e; t)|^2, \quad (15)$$

where $p(e)$ is the probability of finding environment e . This treatment differs fundamentally from the evaluation of incoherent excitation, where sets of quantum states are treated as a single energy level. It is not always appreciated that one cannot use an average Rabi frequency to somehow represent an average molecule. STIRAP is exceptional, because unlike processes that rely on details of Rabi oscillations, if STIRAP works for the weakest transition in the sum then it works for all cases. The discussion in the Appendix relates to the evaluation of the Rabi frequency of $\mathbf{W}(e; t)$ for individual magnetic sublevels of the degenerate ground vibration level of a diatomic molecule. Observations as in Eq. (15) average over those results.

III. EXPANDING THE EXPERIMENTAL BASIS AND FIRST APPLICATIONS

In this section, we comment on the further systematic development of STIRAP, mainly but not exclusively at

Kaiserslautern, that followed the initial presentation of the concept. Complete coverage of that work is not intended here. A concise review of the essence of STIRAP was given by Bergmann *et al.*,¹⁸ while a presentation with a limited amount of math involved can be found in the review of Vitanov *et al.*²⁰ A rather complete review of the experimental and theoretical work until 2001 is given in Vitanov *et al.*¹⁹ A discussion of the pre-history of STIRAP, with a detailed definition, appears in Shore.²³ The first experimental work employing STIRAP outside Kaiserslautern is, to the best of our knowledge, the work by Pillet *et al.*³² who demonstrated population transfer between hyperfine levels of the Cs atom.

A. STIRAP and reaction dynamics

The first application of STIRAP to reaction dynamics was reported in 1992. Dittmann *et al.* studied the reaction $\text{Na}_2(v'') + \text{Cl} \rightarrow \text{NaCl} + \text{Na}^*$ and monitored the variation of the total rate of $\text{Na}(3p)$ formation in a crossed beam experiment. The Cl beam emerged from a discharge and crossed a supersonic beam of Na_2 at a right angle. Changes of the sodium D-line emission were observed as the vibrational excitation of the Na_2 molecules was varied. Although the majority of the data from this experiment were taken using vibrational excitation by Franck-Condon pumping, some crucial data were obtained with vibrational excitation by STIRAP. The results revealed a linear increase of the rate of $\text{Na}(3p)$ formation with vibrational excitation up to $v'' = 19$.

In another experiment, Külz *et al.*³³ looked at the vibrational dependence of the rate of negative ion formation through dissociative electron attachment in the process $\text{Na}_2(v'') + e \rightarrow \text{Na} + \text{Na}^-$. In that work, application of STIRAP was essential to unambiguously determine the location of crossing between the potential energy curves for the $\text{Na}_2 + e$ and the $\text{Na} + \text{Na}^-$ systems, which was found to lie between the energy of the $v'' = 11$ and $v'' = 12$ levels of Na_2 .

Another early application of STIRAP to collision dynamics is the work of Kaufmann *et al.*³⁴ who studied the variation of the rate of the dissociative attachment process $\text{Na}^{**} + \text{Na}_2(v'') \rightarrow \text{Na}^+ + \text{Na} + \text{Na}^-$ with the vibrational excitation of the Na_2 molecule.

B. STIRAP with pulsed lasers and the relevance of transform-limited bandwidth

The initial plan for using the concept of STIRAP aimed to study reactions of small molecules which are abundant in the atmosphere. The first electronically excited states of most relevant molecules require excitation by UV lasers necessitating suitable UV radiation for such experiments. Because there were no sufficiently powerful cw-lasers yielding radiation in the UV, it was necessary to use frequency conversion of lasers with pulses in the range of a few ns.

A crucial difference between ns-range pulsed lasers and cw lasers relevant to STIRAP is the presence of substantial phase fluctuations in the former. STIRAP is not sensitive to absolute phases of either field but adiabatic evolution is impeded when there are changing phase differences during the pulse sequence. These fluctuations induce non-adiabatic

transitions out of the dark state into lossy adiabatic states. When both radiation fields have a Fourier-transform limited spectral profile, there are no phase fluctuations. Spectral profiles broader than the transform limit indicate undesirable phase fluctuations. These must be small for STIRAP to succeed.

Results of detailed simulation studies based on a model that treated pulsed-laser fields subject to phase fluctuations showed³⁵ that efficient STIRAP-induced transfer is possible with such noisy pulses but higher laser power is needed than with transform-limited pulses (purely coherent excitation) to overcome the consequences of phase fluctuations, as one would expect for an adiabatic process. Another important result of that work was the finding that with decreasing pulse width (wanted for higher intensity and consequent higher efficiency of the non-linear conversion from visible to UV radiation), more pulse-energy is required. The relationship between squared peak Rabi-frequency $|\Omega_{\max}|^2$ and pulse duration T for transform-limited pulses is, from (13),

$$|\Omega_{\max}|^2 T \geq 100/T. \quad (16)$$

When, for example, a pulse energy of 0.1 mJ suffices for efficient transfer when the pulse length is 10 ns and the radiation shows a transform-limited spectral profile, the required energy increases to 100 mJ when the pulse width is only 10 ps. At such high power multi-photon excitation, dissociation and ionization processes are likely to be dominant and efficient transfer is no longer possible. For pulses much shorter than 1 ps, the conditions for adiabatic evolution are very unlikely to be fulfilled.

The cost of overcoming pulse noise is quantified by an extension of Eq. (16) that includes the consequences of phase fluctuations, studied by Kuhn *et al.*³⁵ From the version of the formula given by Vitanov *et al.*,¹⁹ we obtain the adiabaticity condition on pulse fluence that replaces Eq. (16) for a noisy laser,

$$|\Omega_{\max}|^2 T \geq \left[1 + \frac{\Delta\omega}{\Delta\omega_{TL}} \right] \frac{50}{T}. \quad (17)$$

Here, $\Delta\omega$ is the actual bandwidth and $\Delta\omega_{TL}$ is the Fourier-transform limited width for a pulse of duration T .

The work of Kuhn *et al.*³⁵ showed that it is difficult to achieve efficient STIRAP when pulse durations are substantially shorter than 1 ns and when the pulse bandwidth exceeds the related transform limit by much more than a factor of 2. In fact, STIRAP has been successfully implemented with pulsed lasers having durations of the order of 10 ns, as documented in Refs. 36–38.

Shapiro and coworkers³⁹ suggested a way to use a series of femtosecond pulses, stretched out over about a picosecond, to induce STIRAP-type transfer, a technique they named piecewise adiabatic passage (PAP). Each pair of *S* and *P* pulses from the pulse train transfers a small fraction of the population from the initial to the target state but the interaction is sufficiently weak that there is no detrimental multi-photon excitation or ionization. Because the process is completed during a time interval shorter than the lifetime of the intermediate state, the needed coherence is maintained within the atomic system between successive femtosecond pulses. That concept was

successfully demonstrated experimentally for transfer between atomic states of rubidium⁴⁰ and for transfer into a superposition of atomic states in potassium.⁴¹ However, attempts to implement the PAP-scheme for a molecule (iodine) failed.⁴²

C. Further consequences of noise for the STIRAP process

Because it relies on coherent excitation, STIRAP works best for radiation with transform-limited pulses. When cw lasers are used, it is the spatial profile of the beam, converted into a time dependence (because particles travel across the laser beams) that determines the time variation of the Rabi frequency.

In recent years, radiation from diode lasers has often provided the STIRAP pulses. These typically employ a feedback stabilization scheme to reduce the bandwidth.⁴³

Those lasers exhibit a characteristic frequency distribution comprising a narrow central part on a broad background pedestal. Although typically 95% or more of the total intensity is within the narrow feature, the broad spectral pedestal may have a significant influence. As shown by Yatsenko *et al.*,⁴³ increasing the intensity for such a laser will not necessarily reduce the nonadiabatic losses and thus allows higher transfer efficiency. Instead, beyond an optimum intensity, the transfer efficiency decreases. These theoretical results are consistent with observations of experimental results from the Nägerl laboratory in Innsbruck.⁴⁴

D. STIRAP with multiphoton transitions: Consequences of the AC Stark shift

Because pulsed laser radiation is much more readily available in the visible spectral range than the UV, Bergmann hoped that STIRAP transfer could be implemented for molecules with high-lying electronic states, such as O₂ and N₂, by two-photon coupling of the initial and intermediate state, followed by either one-photon or two-photon coupling of the intermediate and the target state. A detailed theoretical analysis^{45,46} and experiments⁴⁷ showed that it was possible to have such a “2 + 1” STIRAP, called stimulated hyper-Raman adiabatic passage (STIHRAP), with a 2-photon transition driven by the *P*-laser and 1-photon transition by the *S*-laser. However, the process lacked an essential feature that makes STIRAP so successful, namely, insensitivity to small variation of relevant parameters (robustness).

The problem lies with the dynamic Stark-shift.^{46,48–50} This shift of energy levels originates with interaction of the *P*- and *S*-radiation fields with a host of nonresonant states. When the *P* and *S* lasers are tuned to their individual single-photon resonances, the Stark shift induced by the radiation has negligible effect on the three-state dynamics, including the maintenance of adiabatic following. However, when the interaction originates with a two-photon transition, there is an inevitable accompanying time-dependent Stark shift (which is also a two-photon process). As shown in Ref. 46, the detrimental consequences of the Stark shift can be minimized, but not eliminated, by a suitable small static-detuning of the laser frequency from the two-photon resonance.

Both the two-photon Rabi frequency and the Stark shift depend linearly on the intensity. Reducing the laser power does not help avoiding the detrimental consequences of the Stark shift because not only the Stark shift but also the two-photon coupling is reduced. The Stark-shift induced two-photon detuning adds an excited-state component to all adiabatic eigenvectors, thereby adding spontaneous emission loss. Lossless transfer from the initial to the final state is then no longer possible.

E. Adiabatic transfer through the continuum

In the adiabatic limit, the intermediate state of STIRAP is not populated, and thus, there occurs no population loss by spontaneous emission from the intermediate state. That observation leads one to consider the possibility of lossless population transfer when the intermediate state is in a continuum, as shown in Fig. 1(c).

Theoretical work by Carroll and Hioe⁵¹ suggested that efficient STIRAP transfer through the continuum should indeed be possible. However, it was shown in subsequent work⁵² that the model of Carroll and Hioe⁵¹ was inadequate for properly treating the radiative interaction with a continuum. Because typically the coupling of a bound state to the continuum is much weaker than the coupling between two bound states, and thus the intensity of the *P* and *S* lasers must be high, the off-resonant Stark-shift is not negligible, just as with two-photon coupling between bound states. Because there is a delay between the *P* and *S* interactions, the Stark shift varies with time and the transfer state (see Sec. II E) necessarily acquires a contribution from the continuum, although this may be small. The main limitation is actually imposed by the (incoherent) loss because the final level is ionized by the pump laser radiation. Nevertheless, Peters *et al.* have shown⁵³ that coherent transfer between the 2s and 4s states of He is possible (of the order of 20%) when coupling occurs through the photoionization continuum. Strictly speaking, such a process is not STIRAP, but STIRAP-inspired.²³

F. Stark-chirped rapid adiabatic passage (SCRAP): Making use of the Stark shift

As discussed above, the Stark shift induced by the off-resonant radiative interaction may prevent the realization of very high transfer efficiency by STIRAP. That observation inspired the development of another powerful transfer scheme named Stark-chirped rapid adiabatic-passage (SCRAP). In that scheme, an additional laser, not in resonance with any transitions (and typically at a wavelength in the infrared), induces Stark shifts. Whereas in traditional rapid adiabatic passage (RAP),^{20,23} the laser is chirped across resonance, by contrast in SCRAP, the resonance is chirped across the laser frequency. The pulse energies and time delay are designed such that curves of diabatic energies vs. time have two crossings, while those of adiabatic eigenvalues vs. time have two avoided crossings. At one of these, the adiabatic curves are well separated and evolution remains adiabatic, whereas at the other, the curve separation is small (or zero) and evolution is diabatic. At that time, there occurs a change of guiding adiabatic state.^{54,55}

In the three-state version of that scheme,⁵⁰ the intermediate state receives some population (that is why the name includes the term “rapid”: the process needs to be completed during an interval shorter than the relevant electronic lifetime) but proper design of the strength and sequence of the interactions minimizes the intermediate state population and thus efficient transfer from the initial to the final state is possible.⁵⁶

A variant of that method called stimulated adiabatic Raman passage (SARP) has been successfully implemented experimentally by Zare and coworkers.⁵⁷ Their work demonstrated very high transfer efficiency from the vibrational ground state $v'' = 0$ to $v'' = 1$ of H₂.

G. STIRAP in multistate systems and the consequences of high level-density

STIRAP was introduced as a method for transferring population between well isolated, possibly non-degenerate, quantum states. Although not mentioned explicitly in Ref. 1, the early work showed transfer of the population of an entire set of Zeeman sublevels of a specific rotational level. For example, with linear polarization and initial nonzero angular momentum $j'' \neq 0$, one deals with several independent three-state systems, each one labeled by the magnetic quantum number *M*. The transition dipole moment depends on *M* and so does the Rabi frequency. When the adiabaticity criterion of Sec. II D is satisfied for the sub-system with the smallest transition dipole moment, it is satisfied for all other three-state systems involved and all the populations in a rotational level are transferred.

A question that was also considered during the early days of STIRAP was how complex can a molecule be and still undergo STIRAP? There are several concerns to be considered. With increasing complexity of the molecule, there is an increase in the number of quantum states and a decrease in their energy separation. The increasing number of states reduces, on average, the transition dipole moment between any pair of states. In turn this means that, in order to maintain satisfactory Rabi frequencies for adiabaticity, the radiation must be more intense. Furthermore, a treatment of the process as a transfer between three states is no longer valid: modeling must include many states with closely spaced energies. Radiative interactions with the numerous other states will introduce Stark shifts that cause a detrimental two-photon detuning. Furthermore, and possibly even more important, many single or multi-photon excitation processes become possible, and these will diminish the transfer efficiency.

A series of papers^{27,58,59} found quantitative answers to the problem by studying the transfer from the metastable state ³P₀ of neon to specific Zeeman sublevels of ³P₂. The theoretical work^{58,59} was verified by experiments.²⁷ This work demonstrated how the coupling could be directed to one or more of the Zeeman sublevels of the target level *J* = 2 by proper choice of the polarization of the *P* and *S* fields. Moreover, adjustment of the strength of the applied magnetic field altered the energy spacing of the Zeeman sublevels of *J* = 2 from zero to a maximum. To understand the observed population transfers and their dependence on polarizations and Zeeman splittings, it was necessary to evaluate the adiabatic eigenvalues for the full set of states as a function of time for a range of controllable

parameters (strength of B-field, intensity of lasers, etc.). The curves of adiabatic energies as a function of time, though often complicated, showed pathways for the system leading from the eigenvalue of the initial state to eigenvalues of possible final states. In the simplest situations, there occurs a single adiabatic curve (that of a dark state) joining two endpoints (the energies of the initial and the desired target state). By ensuring adiabatic evolution, the experimenter can cause the system to follow this path, thereby achieving exclusive population of the desired final state. In other situations, a transfer path from the initial to the target state may not even be available.

From this work came an important general conclusion: as long as the initial state and target state are separated from any radiatively coupled neighboring states by more than the maximum $\Omega_{\text{rms}}(t)$, efficient population transfer is possible.

The most complex molecule for which successful population transfer by STIRAP has been experimentally demonstrated is, to the best of our knowledge, the work by Halfmann and Bergmann³⁷ on SO₂. This work showed complete population transfer between the vibrational levels (0,0,0) and (9,1,0) of the electronic ground state using pulsed laser radiation in the near UV.

There have been a number of suggestions for using STIRAP with molecules that have a more complex structure than SO₂. Such work approximates the energy-level structure of the molecule by a few-state model for which STIRAP has been simulated. However, for a calculation to have any predictive value, the model must include all radiatively coupled states neighboring the initial and final states, as well as states coupled by multiphoton transitions to one of the states 1, 2, or 3. In most cases, a few-state model is inadequate to judge the feasibility of STIRAP for a polyatomic molecule. In fact, Jakubetz⁶⁰ has shown by extensive simulation that STIRAP may be possible for the HCN molecule, although the characteristic and essential robustness are lost entirely. His modeling included up to about 450 vibrational levels, with energies and transition dipole moments taken from high-quality *ab initio* calculations.

Another interesting variant of transfer in a multi-state system through coupling of more than two lasers (straddle-STIRAP) was suggested by Malinovsky and Tannor⁶¹ and was further studied by Vitanov *et al.*⁶² Straddle-STIRAP envisions, e.g., the transfer within a 5-state chain that has a “letter-M” linkage pattern, as shown in Fig. 1(h). In addition to the *P* and *S* Rabi frequencies that connect with initial and final states, there are intermediate links *Q* (possibly induced by a single laser frequency but with different polarizations to determine which two states are coupled). The laser *S* precedes but overlaps with *P* in the typical STIRAP way. The *Q*-fields overlap both of these, as shown in frame (g). The three intermediate states, coupled by the *Q* fields, can be replaced by three “dressed states,” to which the *P* and *S* fields link, as shown in frame (i). This pattern is a variant of the conventional STIRAP lambda linkage, and population transfer takes place but intermediate state 3 acquires some temporary population, an amount that decreases with increasing intensity of the *Q* lasers.⁶² The straddle-STIRAP concept has been experimentally implemented successfully in the work by Danzl *et al.*⁴⁴ to form Cs₂ molecules in their lowest-energy quantum state (see also Sec. IV) starting from very weakly bound states of a Cs₂ (Feshbach) molecule.

H. Coherent superposition of states prepared and controlled by STIRAP

Preparation of a well-controlled coherent-superposition state is another one of the many interesting applications of STIRAP. When the intermediate state links to two target states rather than just one, there are two excitation paths available from the initial state. If the two target states are degenerate Zeeman sublevels, the needed secondary links can be provided by a single-frequency field that has two polarization components, see Figs. 1(e) or 1(f). Vewinger *et al.* have given a detailed analysis, with experimental demonstration, of the preparation of superpositions of degenerate sublevels.^{63–66} More generally, the linkage to multiple final states requires lasers of different frequencies. The simplest example is the “tripod linkage” of four states with three fields.⁶⁷ Figures 1(d)–1(f) show an example, appropriate to the Vewinger work, in which the *S* field links the excited state to two degenerate Zeeman sublevels. By adjusting the relative strength of the two *S* fields, an experimenter can produce a superposition of the two sublevels with predetermined ratio of population and phase differences.

As with all tripod linkages, the linkage pattern of Figs. 1(d)–1(f) has two degenerate adiabatic eigenvectors that lack excited-state components (they are dark, population trapping states) and span a two-dimensional Hilbert subspace. Consequences of this degeneracy have been discussed by Unanyan *et al.*^{67,68} and many others, e.g., Refs. 69–73.

I. STIRAP applications in matter-wave optics

The work by Marte *et al.*⁷⁴ was the first to recognize the high potential of STIRAP for matter-wave optics. They proposed an application of that scheme to create a new kind of beam splitter for matter waves. This work stimulated several experiments along those lines: the demonstration of a deflector for cesium atoms by transferring a momentum of $8\hbar k$ from the light field to the atom,⁷⁵ the development of a beam splitter for He-atoms,⁷⁶ and even a matter-wave interferometer for cesium atoms.⁷⁷

Later, Theuer *et al.*⁷⁸ developed a variable beam-splitter for Ne⁺ atoms in a highly collimated supersonic beam, based on the tripod-STIRAP scheme.⁶⁷ In that scheme, the population of the metastable state ³P₀ of Ne is coupled by linearly polarized light (the *P* field) to an intermediate state of ³P₁, which in turn is coupled to the *M* = +1 and *M* = −1 Zeeman sublevels of the ³P₂ level by circular polarized radiation (the *S* fields), thereby preparing the atom in a coherent-superposition state. If the two circularly polarized fields approach the atom from opposite directions, then the photon momentum transferred to the atom in the *M* = +1 and *M* = −1 states is also in different directions, leading to a spatial separation of the atoms in the two Zeeman sublevels as they further propagate in the atomic beam. A very interesting feature of that scheme is the option to smoothly vary the splitting ratio from 0:1 to 1:0 by controlling the sequence of interactions of fields with the atoms. If the two *S* fields are of equal intensity and there is no mutual time-delay in their interaction with the atom, the result is a 50:50 beam splitter. Theuer *et al.*¹⁸ demonstrated with a more elaborate arrangement of laser beams a mirror-type reflection

of a neon beam in which the atoms entered and left the radiation fields in the same Zeeman sublevel but acquired a transverse momentum of $8\hbar k$.

IV. RECENT STIRAP EXPERIMENTS WITH ATOMS, MOLECULES, AND BEYOND

In Subsections IV A–E, we discuss a few interesting recent experiments that use STIRAP, carried out in labs other than in Kaiserslautern. Section IV F lists further examples to document the variety of STIRAP applications.

A. STIRAP in ultracold atoms-molecule conversion

Laser cooling has had a major impact on atomic physics by making possible atom and ion trapping, quantum degenerate gases, and quantum information processing with atoms and ions. Unfortunately, laser cooling methods are not readily applicable to molecules because of their rovibrational structure and the ensuing absence of closed two-level transitions. A major route to ultracold molecular gases is by association of ultracold atoms. Soon after the first creation of Bose-Einstein condensates (BECs) in the gas phase, it was proposed to use two-color photoassociation with counterintuitively ordered pulses.^{79–81} The challenges in the application of STIRAP to such atoms-molecule conversion is the nonlinearity of the dynamics (the dependent variables—the field amplitudes—enter the differential equations as products, i.e., not linearly) and the smallness of the free-bound dipole matrix elements. It has been concluded⁸¹ that such a STIRAP-like atoms-molecule conversion could still be possible, thanks to Bose-enhancement of the free-bound couplings.

Over the last decade, an alternative technique to associate atoms into molecules, again using STIRAP, has proved very successful. This approach uses a Feshbach resonance between the colliding ultracold atoms and a quasibound molecular state of the desired molecule. First, an appropriate magnetic field ramp near a Feshbach resonance converts atoms very efficiently into (Feshbach) molecules. The Feshbach molecules are usually unstable because they reside in very weakly bound states close to the dissociation threshold. Therefore, the creation of Feshbach molecules is followed immediately by a STIRAP transfer to the rovibrational ground state. After a proof-of-principle experiment of this technique by Winkler *et al.*⁸² in Rb_2 molecules, Danzl *et al.*⁸³ converted Cs_2 Feshbach-molecules to molecules tightly bound by more than 1000 wave numbers. Then, Lang *et al.*⁸⁴ produced ultracold $^{87}\text{Rb}_2$ molecules in the rovibrational ground state of their triplet manifold with over 90% efficiency. At about the same time, Ni *et al.*⁸⁵ produced by the same method an ultracold dense gas of $^{40}\text{K}^{87}\text{Rb}$ heteronuclear polar molecules in both their singlet and triplet rovibrational ground states. Recently, also the formation of deeply bound ultracold $^{84}\text{Sr}_2$ molecules has been reported.⁸⁶ We also mention the work by Danzl *et al.*⁴⁴ on Cs_2 and an all-optical experiment by Aikawa *et al.*⁸⁷ on $^{41}\text{K}^{87}\text{Rb}$, each producing molecules in their rovibrational ground state by photoassociation through STIRAP. Such experiments require a detailed spectroscopic analysis of the system in order to

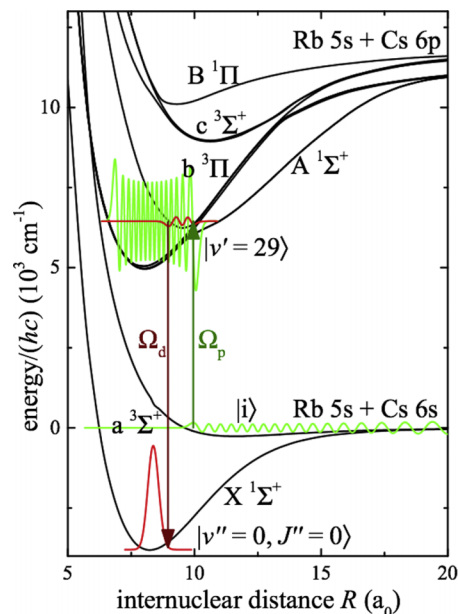


FIG. 4. STIRAP scheme for the formation of ultracold RbCs molecules. The transfer from the Feshbach state $|i\rangle$ at threshold to the rovibrational ground-state level $|v''=0, J''=0\rangle$ involves the $v'=29$ level belonging to the $b^3\Pi(\Omega=1)$ electronically excited state. The red and green solid lines indicate the wavefunctions that are coupled by the STIRAP lasers P (called “pump”) and S (called “dump”) with Rabi frequencies Ω_p and Ω_d , respectively. Reprinted with permission from Fig. 1 of Takekoshi *et al.* Phys. Rev. Lett. **113**, 205301 (2014) Copyright 2014 by APS.

find suitable levels for the STIRAP process (see, e.g., Schulze *et al.*⁸⁸)

Very recently, Takekoshi *et al.* reported the creation of ultracold dense samples of RbCs molecules in their rovibrational and hyperfine ground state.⁸⁹ Figure 4 shows the excitation scheme and Fig. 5 shows examples of their population transfer.

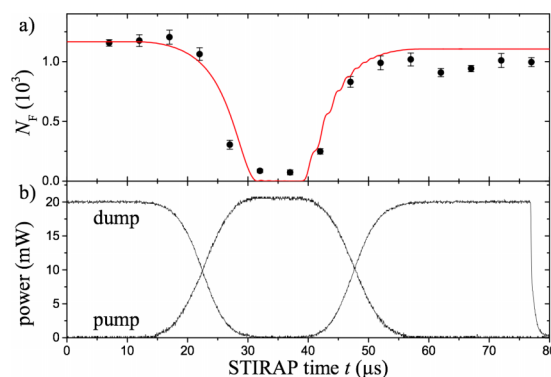


FIG. 5. Timing of the laser pulses (lower panel) and evolution of the population in the Feshbach state (upper panel) for the STIRAP scheme of Fig. 4. After the first STIRAP process, the Feshbach molecules disappear. A second STIRAP process drives the population from the lowest-lying molecular RbCs level back to the Feshbach state (for detection). The initial population of that state is nearly restored. The one-way STIRAP efficiency is 90%. The red curve of the upper frame shows the result of a model calculation which does not include deviations from perfect experimental conditions, like a pedestal in the spectral line shape, and with imperfect overlap between the laser beams and the molecular sample. From Fig. 2 of Takekoshi *et al.* Phys. Rev. Lett. **113**, 205301 (2014). Copyright 2014 by APS.

B. Single-atom cavity quantum electrodynamics (QED)

The first unconventional implementation of STIRAP beyond laser-driven atoms and molecules was proposed by Parkins *et al.*⁹⁰ They recognized the potential of STIRAP in cavity QED for creation of a well defined photon number (Fock) state of the cavity mode. Parkins *et al.*⁹⁰ also proposed to create coherent superpositions of Fock states by mapping a coherent superposition of Zeeman atomic sublevels to the cavity field.

The quantized field of the single-mode cavity provides the Stokes coupling (a vacuum Rabi frequency) denoted by $g(t)\sqrt{n+1}$, where n is the number of photons in the cavity mode and $g(t)$ is the coupling strength in a vacuum, $n=0$. The pump coupling is produced by a laser field, which is focused inside the cavity but slightly off the cavity axis, as shown in Fig. 6. Therefore, the pump and Stokes fields partly overlap, but being suitably displaced in space, they are seen as a counterintuitive pulse sequence by an atom falling from above.

Because the Stokes cavity field is quantized, with photon-number eigenstates $|n\rangle$, the dynamics is described by the combined atom-photon states $|\psi, n\rangle = |\psi\rangle|n\rangle$. With the RWA, only three such atom-field states are coupled: $|\psi_1, n\rangle$, $|\psi_2, n\rangle$, $|\psi_3, n+1\rangle$. The dark atom-field state corresponds to energy $E_n = \hbar\omega$, with ω being the frequency of the cavity mode, and it reads

$$|E_n\rangle = \frac{2g(t)\sqrt{n+1}|\psi_1, n\rangle - \Omega_P(t)|\psi_3, n+1\rangle}{\sqrt{4(n+1)g(t)^2 + \Omega_P(t)^2}}. \quad (18)$$

The atoms pass through the cavity and interact first with the Stokes cavity field and then with the pump laser field. In the adiabatic limit, complete transfer $|\psi_1, n\rangle \rightarrow |\psi_3, n+1\rangle$ is achieved in a decoherence-free fashion, without populating the decaying excited state $|\psi_2, n\rangle$ at any time. For $n=0$ (empty cavity initially), a single-photon state is created out of the vacuum after the atom passes through the cavity. If the atom arrives in a coherent superposition of Zeeman sublevels, then cavity-STIRAP may produce a coherent superposition of Fock states. The transfer of coherence from an atom to a field mode is reversible; likewise, it allows the mapping of cavity fields onto atomic ground-state coherence, which has been suggested as a method for measuring cavity fields.⁹²

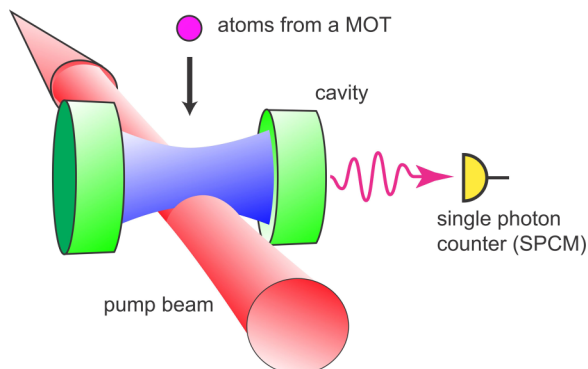


FIG. 6. Artistic view of the experimental setup used for demonstration of vacuum-STIRAP. Reprinted with permission from Fig. 4 of Hennrich *et al.* Phys. Rev. Lett. **85**, 4872–4875 (2000). Copyright 2000 by APS.

Because of the quantized cavity field, the usual adiabatic condition becomes, for the pump field, $\Omega_P T_P \gg 1$; for the Stokes field, it is $2g_{\max} T(n+1) \gg 1$. A thorough analysis in the presence of cavity losses with rate κ and spontaneous emission of the intermediate atomic state $|\psi_2\rangle$ with rate γ relates the adiabatic condition to the strong-coupling cavity regime, $g(t)^2 \gg \kappa\gamma$.

Cavity-STIRAP has been demonstrated and used in numerous experiments by Rempe and co-workers. Cavity-STIRAP for stimulated generation of single photons by single cold rubidium atoms passing through a high-finesse cavity was demonstrated experimentally by Hennrich *et al.*⁹¹ Kuhn *et al.*⁹³ constructed a deterministic single-photon source in a similar experiment, while Legero *et al.*⁹⁴ observed quantum beats of two single photons. Hennrich *et al.*⁹⁵ studied the statistics of the photons emitted by a single atom and observed the transition from antibunching to bunching. Wilk *et al.*⁹⁶ produced a stream of single photons with alternating circular polarization by alternately exposing the atom to laser pulses of two different frequencies and polarisations. Wilk *et al.*⁹⁷ built the basic element of a distributed quantum network: an atom-photon quantum interface that entangled a single atom with a single photon and mapped the quantum state of the atom onto a second single photon, thereby producing an entangled photon pair. Nölleke *et al.*⁹⁸ demonstrated teleportation of quantum bits between two single atoms in distant laboratories with a fidelity of 88%.

C. STIRAP and quantum-information processing

Because of its insensitivity to dissipation from the intermediate state, STIRAP has been a popular tool in quantum information in recent years. To this end, we mention the use of STIRAP for efficient qubit manipulation⁹⁹ and detection¹⁰⁰ in trapped calcium ions.

STIRAP has proved to be an efficient and robust tool for creation and manipulation of coherent superpositions of qubit states, which are of crucial importance in quantum information. If the structure and timing of the S and P pulses are such that the ratio Ω_S/Ω_P does not go to zero at late times but instead reaches a finite predetermined value, then adiabatic following will produce a coherent superposition of initial- and final-state probability amplitudes, a process termed *fractional STIRAP* and demonstrated by Vewinger and Lvovsky.¹⁰¹ If the two populations are equal (a population ratio of 0.5), the process is termed *half-STIRAP*. This has been demonstrated by Danzl *et al.*⁸³ It has been used recently in two experiments on demonstration of a dressed-state qubit in microwave and rf-driven ytterbium ions in a magnetic gradient trap.^{102,103} Figure 7 demonstrates the idea (top) and the experimental data (bottom). The four-state system is driven by microwave ($|0\rangle \leftrightarrow |-1\rangle$ and $|0\rangle \leftrightarrow |+1\rangle$) and radiofrequency ($|0'\rangle \leftrightarrow |-1\rangle$ and $|0'\rangle \leftrightarrow |+1\rangle$) fields. Instead of bare atomic states, the qubit is constructed from state $|0'\rangle$ and the dressed state $|D\rangle$, which is the dark superposition of the sublevels $|\pm 1\rangle$. The dressed qubit is insensitive to magnetic field fluctuations, and its coherence time exceeds the one of the bare-state qubit by three orders of magnitude, from about a millisecond to a few seconds, cf. Fig. 7 (bottom). Half-STIRAP is used twice: to populate the

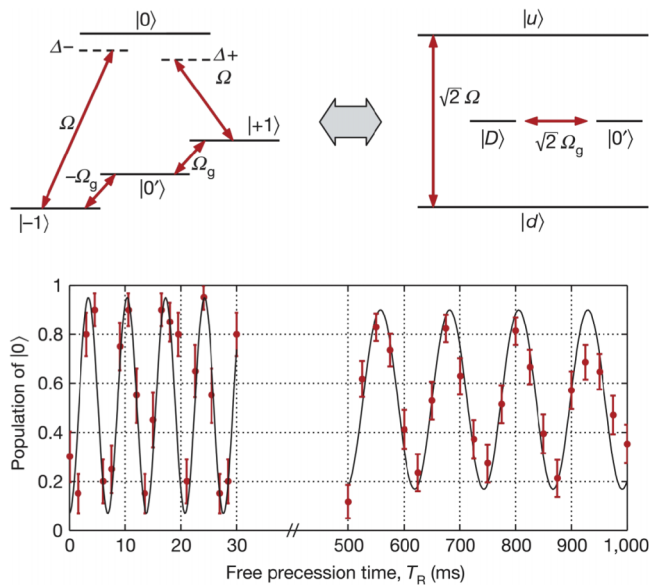


FIG. 7. Upper plot: level scheme in the experiment by Timoney *et al.*¹⁰² Lower plot: Ramsey fringes verifying the coherence of the dressed qubit $\{|0'\rangle, |D\rangle\}$. Reprinted with permission from Figs. 1 and 3 of Timoney *et al.* Nature **476**, 185–188 (2011). Copyright 2011 by Nature Publishing.

dressed state $|D\rangle$ initially and then to drive it back to one of the bare state for detection in the end.

Various techniques have been proposed to create entangled collective states of multiple qubits by using STIRAP. Unanyan *et al.*¹⁰⁴ proposed to use STIRAP to create an entangled state of two qubits in a robust fashion, with the relative phase of the superposition being of geometric nature. Linington and Vitanov¹⁰⁵ proposed a method to create highly entangled Dicke states of trapped ions by multistate STIRAP. Dicke states of up to four ions have been demonstrated in an experiment by Noguchi *et al.*¹⁰⁶ by a variation of multistate STIRAP, in which the intermediate states are phonon Fock states.

Of particular interest in quantum information has been the tripod system because of its two dark states. STIRAP-like processes allow one to generate single-qubit^{68,72} and two-qubit^{107–109} geometric phase-gates protected from decoherence. Moreover, tripod-STIRAP has been proposed for observation of the elusive “zitterbewegung” effect in ultracold neutral atoms.¹¹⁰

D. STIRAP in doped crystals

In the 1990s, STIRAP and coherent manipulation of quantum states in general have been demonstrated exclusively in atomic media in the gas phase. During the last decade, some particular atom-like solid-state systems have attracted significant attention as promising candidates for coherent light-matter interaction, especially in the context of quantum information processing because solid state is the most appealing physical platform of a quantum computer. Atom-like examples are quantum dots,^{111,112} color centers,¹¹³ and rare-earth-ion doped solids.^{114,115} The rare-earth-metal materials offer suitable properties for coherent manipulation for they possess narrow optical linewidths and long decoherence times.

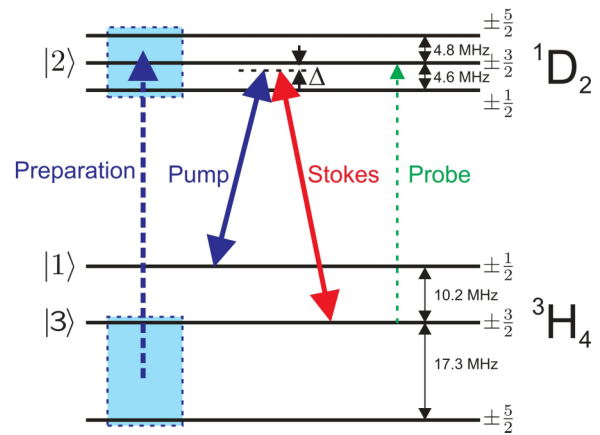


FIG. 8. Level scheme for the implementation of STIRAP in $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ crystal by Klein *et al.*¹¹⁸ Reprinted with permission from Fig. 4 of Klein *et al.* Phys. Rev. A **78**, 033416 (2008). Copyright 2008 by APS.

These media combine the advantages of solids (i.e., large density and scalability) with the advantages of free atoms in the gas phase (i.e., long coherence times and spectrally narrow optical transitions). Following an early experiment by Goto and Ichimura,¹¹⁶ Klein *et al.*^{117,118} conducted a thorough experimental study of STIRAP between hyperfine levels of praseodymium ions in a cryogenically cooled $\text{Pr}^{3+}:\text{Y}_2\text{SiO}_5$ crystal, see Fig. 8.

Because of the huge inhomogeneous broadening of the medium (of the order of 10 GHz), a narrow spectral pit is initially prepared by spectral hole burning and optical pumping. Hence, only Pr^{3+} ions within this spectral pit are involved in the interaction thereby resembling (spectrally) atoms in a gas phase. Nearly 100% population transfer efficiency between sublevels $|\pm\frac{1}{2}\rangle$ and $|\pm\frac{3}{2}\rangle$ of the $^3\text{H}_4$ hyperfine level has been reported on two-photon resonance by counterintuitively ordered pulses as seen in Fig. 9. Off two-photon resonance, (incoherent) population transfer occurs mainly due to optical pumping by the resonant pump pulse alone.

Klein *et al.*¹¹⁷ have also observed bright-state STIRAP (b-STIRAP,^{23,117,119}) which operates with intuitively ordered pulses off two-photon resonance, already observed (in the gas phase) in the original STIRAP work,¹ and further discussed by Vitanov and Stenholm,¹²⁰ see the right-hand side of the bottom frame of Fig. 9. In that case, the efficiency is lower than in STIRAP (left part) because the process proceeds by means of a bright state, which includes a component of the decaying state. Population transfer is still possible if the lifetime of the intermediate state is much longer than the interaction time with the lasers or if the laser frequencies are detuned sufficiently far from resonance with the intermediate state.

E. STIRAP in waveguides (WGs)

One of the major applications of STIRAP outside of atomic and molecular physics has taken place in recent years in WG optics. It is grounded in the formal analogy between the time-dependent Schrödinger equation and the equations describing light propagation in evanescently coupled WGs. An array of N coupled WGs is formally analogous to an N -level

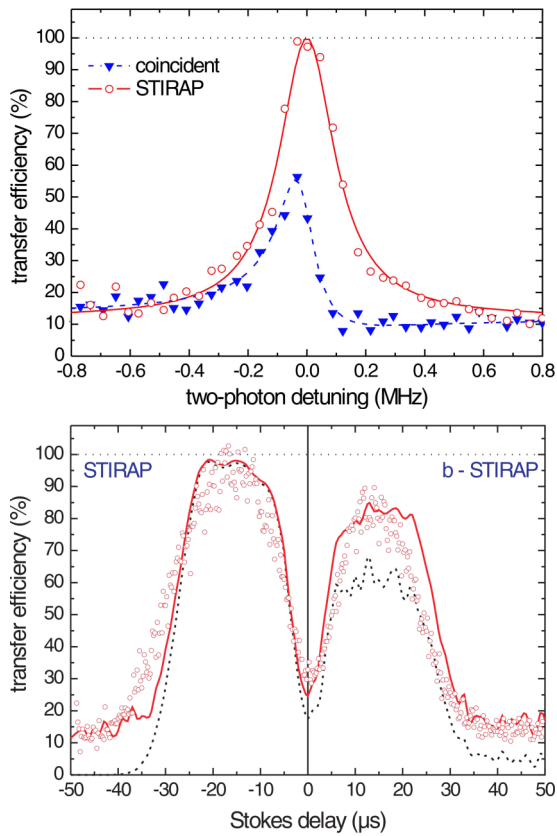


FIG. 9. Experimental demonstration of STIRAP in a doped solid crystal by Klein *et al.*¹¹⁷ Top frame: population transfer efficiency vs the two-photon detuning (pump frequency fixed, Stokes frequency varied) with a peak observed on two-photon resonance. Bottom frame: population transfer efficiency vs pulse delay. Both fields are off resonance by the same detuning $\Delta = 2\pi \times 320$ kHz (see Fig. 8) so that they are still on two-photon resonance. The dashed curve shows the data with the incoherent population transfer contribution excluded. The peak of the left-hand data is interpreted as STIRAP (*S* pulse before *P* pulse); the peak of the right-hand data is interpreted as bright-state b-STIRAP.^{23,117,119} Reprinted with permission from Figs. 2 and 4 of Klein *et al.* Phys. Rev. Lett. **99**, 113003 (2007). Copyright 2007 by APS.

quantum system. The evanescent-field coupling κ between the WGs produces light tunneling between them. Variation of the spatial separation between the waveguides enables variation of the coupling. This spatially varying coupling $\kappa(z)$ corresponds to a time-varying Rabi frequency $\Omega(t)$ in a quantum system undergoing STIRAP. The diagonal elements in the driving matrix—the detunings in a quantum system—are related to the distance between the WGs and their curvature. A variety of WG analogs of quantum optics effects have been proposed and some of them have been demonstrated experimentally. A review by Longhi¹²¹ describes many of these.

Greentree *et al.*¹²² and Eckert *et al.*¹²³ were the first to propose the use of STIRAP for coherent transport by adiabatic passage (CTAP) of matter waves between spatially separated potential wells. Longhi¹²⁴ and Longhi *et al.*¹²⁵ extended this idea to the classical problem of light traveling through an engineered triple-well optical-waveguide structure, as shown in Fig. 10. They demonstrated, both experimentally and with simulation, radiation energy transfer between the two outermost of three WGs that meet within a short interval. At those positions, the coupling between adjacent WGs becomes

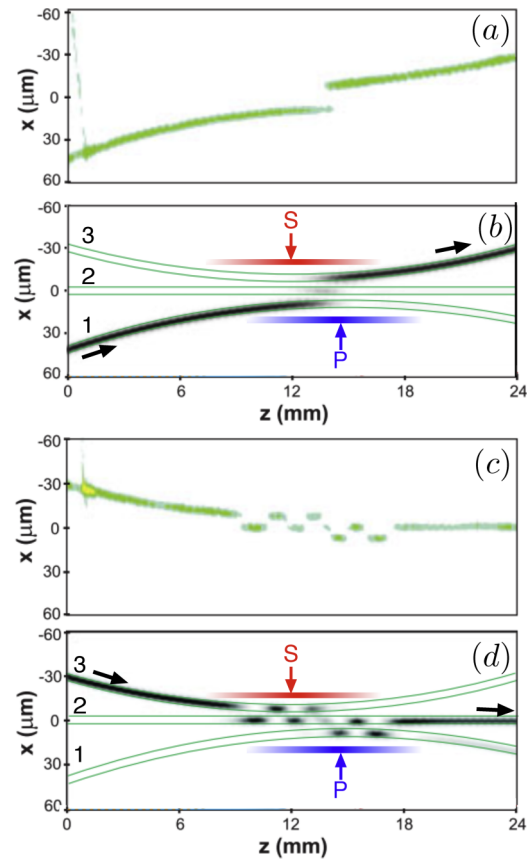


FIG. 10. Experimental data [frames (a) and (c)] and simulation [frames (b) and (d)] of light propagating through a set of three waveguides (upper, middle, and lower) in which there occur brief couplings between adjacent waveguides. The upper two frames, (a) and (b), show couplings that correspond to the “counterintuitive” pulse sequence, producing STIRAP-like transfer of radiation intensity, while the lower two frames, (c) and (d), show couplings that correspond to the “intuitive” interaction sequence leading to Rabi oscillations. Black slanted arrows show the dominant intensities (or populations). Horizontal red and blue lines added to frames (b) and (d) indicate the extent of *S* and *P* pulses (centered at the vertical arrows that mark positions of closest approach). Adapted with permission from Fig. 8 of S. Longhi, Laser Photonics Rev. **3**, 243–261 (2009) (with addition of labels). Copyright 2009 by John Wiley.

strong. Vertical arrows mark the positions of closest approach, where the coupling is strongest. Single mode fields in the three WGs correspond to quantum states 1, 2, 3, and the couplings correspond to the *S* and *P* pulses.

As radiation passes through the WGs (from left to right in the figures), there occurs first an interaction between the upper and middle waveguides, analogous to the *S*-pulse interaction between states 2 and 3 of the quantum system. This is followed by an interaction between the middle and lower waveguides, analogous to the *P* pulse of the quantum system.

In the upper two frames, (a) and (b), the initial conditions are analogous to placing population into state 1. The subsequent occurrence of the *S*-before-*P* interactions is that of STIRAP: radiation intensity transfers completely from the lower to the upper WG. In the lower two frames, (c) and (d), the initial conditions are analogous to placing population into state 3, with the same sequence of interactions. This initial state encounters first the *S* pulse, which begins Rabi oscillations that are continued by the subsequent *P* pulse, through state 2 to

state 1. This is an example of an “intuitive” pulse sequence. With the chosen conditions, the final intensity distribution is concentrated in the middle WG (state 2).

In a following development, Della Valle *et al.*¹²⁶ have demonstrated experimentally the so-called straddle-STIRAP^{61,127} of Figs. 1(g)–1(i) in its dressed-states version.⁶² They have transferred the light between the two outermost WGs in a set of 7 evanescently coupled optical WGs through the 5 intermediate WGs with nearly perfect efficiency, with negligible light intensity in the middle waveguides.

The achromatic nature of multiple-WG STIRAP has been demonstrated experimentally by Ciret *et al.*¹²⁸ in arrays of up to 9 WGs. The effects of nonlinearity on WG-STIRAP have been investigated experimentally by Lahini *et al.*¹²⁹ Finally, a modified version of STIRAP, in which the final state is replaced by a set of states and which produces complete population transfer to a superposition of these states,¹³⁰ has been demonstrated experimentally in a WG structure by Ciret *et al.*¹³¹

F. Other applications of STIRAP

Since we can not cover in this article all the interesting developments and suggestions for the use of the STIRAP method in other contexts, we list below some of the topics together with one selected reference.

- Coherent transport by STIRAP-like adiabatic passage between three quantum dots bypassing the middle one.¹³²
- STIRAP in superconducting nanocircuits.¹³³
- Isomerization reaction HCN-CN_H driven by STIRAP.¹³⁴
- Composite STIRAP (merger of composite pulses with STIRAP for ultrahigh efficiency).¹³⁵
- Mode conversion in waveguides.¹³⁶
- Harmonic generation modified and enhanced by STIRAP.¹³⁷
- Broadband polarisation conversion inspired by STIRAP.¹³⁸
- Various STIRAP analogs in classical physics.¹³⁹
- STIRAP-inspired wireless energy transfer.¹⁴⁰

V. PERSPECTIVES AND SUMMARY

To judge from the rapid increase of relevant publications in the field of atomic, molecular, and optical (AMO) physics or chemistry and beyond, the potential of STIRAP to help solve interesting scientific as well as practical problems is by no means fully explored. Although it is difficult to predict where creativity within the scientific community will take the field, a few lines of expected future developments can be identified.

For instance, relatively little work has been done regarding the challenge that was the motivation to develop STIRAP, namely, the study of the consequences of vibrational excitation on collision dynamics. Despite the very early work with STIRAP^{33,34,141} and the impressive success of methods like SEP (see Refs. 6–10 and Northrup *et al.*¹⁴²), there are many

interesting problems where using the full potential of STIRAP could be beneficial. We give a few examples below.

A. Atmospheric chemistry

A major challenge remains the study of reaction processes of vibrationally excited molecules which are relevant for understanding aspects of the chemistry of the atmosphere, with, e.g., O₂ and N₂ being the most abundant ones. Radicals like OH, which are formed by reactions or photo-dissociation processes, are also relevant. Although much progress has been made in recent years, it is still true that many reactions and energy transfer processes involving highly vibrationally excited species are poorly understood, although they are important for the chemistry of planetary atmospheres.¹⁴³ For instance, the collision processes of OH(*v*'' >> 1) molecules, formed in high vibrational-levels through, e.g., the reaction of ozone and hydrogen, are of interest, cf. Ref. 144 as is the vibrational dependence of the dissociative recombination of O₂⁺ and CO₂⁺, see Ref. 145.

The main problem with the attempt to study such processes derives from the fact that many molecules have their first electronic state at energies that require radiation fields in the ultraviolet or vacuum-ultraviolet (VUV) region of the spectrum to couple them to levels of the ground electronic state. Although such radiation sources are available, their properties are usually unsuitable for the implementation of STIRAP. In most cases, the spectral line width is much larger than the needed (nearly) Fourier-limited bandwidth. Furthermore, most sources are pulsed with pulse length in the range of picoseconds to femtoseconds, if not shorter. Indeed, one of the driving forces for developing radiation sources in the VUV is the very high time resolution which can be realized with them. However, STIRAP being an adiabatic process will not work with ultrashort pulses, see Sec. III B.

Nevertheless, there are many new radiation sources currently under development in Europe and worldwide, including large scale machines such as free-electron lasers,¹⁴⁶ and some of those sources are expected to yield radiation with good coherence properties.

Therefore, it may be possible in the near future to use STIRAP for efficient and selective vibrational excitation of molecules of interest to atmospheric chemistry, such as N₂ or O₂ (but also H₂ and others) and radicals, to a level *v*'' much larger than *v*'' = 1.

We point out that higher lying vibrational levels of the electronic ground state are best accessible by STIRAP when the intermediate level lies in an electronically excited state with a slightly larger equilibrium bond length than the ground state. In that case, one reaches from the ground *v*'' = 0 level the *v*' > 1 in the intermediate state and from there final states with *v*'' >> 1.

As an example, we note that for H₂ nearly all vibrational levels up to the dissociation limit can be reached from *v*'' = 0 when coupling occurs through the B ¹Σ_u⁺ state with λ_P ≈ 100 nm for the transition driven by the P laser.¹⁴⁷ Similarly, nearly all vibrational levels *v*'' for O₂ can be reached via coupling through the B ³Σ_u⁻ electronic state (the Schumann-Runge band).^{148,149} Equally, selective vibrational excitation of,

e.g., N_2 and N_2^+ seems quite possible as soon as narrow-band coherent radiation of sufficient intensity is available in the spectral region 150–100 nm, see Refs. 148 and 149.

B. Numerical examples

In order to encourage doing STIRAP experiments, in particular in spectral regions which have not yet been explored for such work, we here discuss estimates of the intensity I^S or fluence F^S needed to satisfy the adiabaticity criterion for the process. The Appendix discusses the derivation of a formula that provides an estimate of the minimum intensity required to accomplish satisfactory STIRAP. With the choice $S = 1/9$, the basic formula (A2) reads

$$I^S(\text{mW}/\text{mm}^2) = \frac{3.7 \times 10^2}{A_{v''v'}(s^{-1}) (\lambda(\text{nm}))^3 (T(\text{s}))^2}, \quad (19)$$

where, as explained in the Appendix, $A_{v''v'}$ is the band-average Einstein A,^{150–152} λ is the wavelength, and T is the Gaussian width of the Rabi frequency. Equation (19) is to be used for cw radiation. When the radiation is pulsed, the important quantity is the minimum fluence (the time integrated intensity) required to accomplish STIRAP, estimated from the formula $F^S = I^S \times T$. In Table I of the Appendix, we provide, as examples, numerical values for I^S and F^S for the H_2 , O_2 , and NO molecules. With those numbers on hand, it is easy, based on Eq. (19), to estimate I^S or F^S for parameters other than those given.

We emphasize as important consequences of Eq. (19) that I^S

- increases with decreasing $A_{v''v'}$. This is because a smaller decay rate shows weaker coupling and thus, for a given intensity, smaller Rabi frequency;
- increases significantly, as $1/T^2$, with decreasing interaction time T . This is because the transfer process is faster, and thus, larger Rabi frequencies are required for adiabatic evolution. The fluence F^S increases linearly with $1/T$;
- increases also significantly as the inverse cube of the wavelength. This factor originates with the density of free-space photon modes in the calculation of the Einstein A¹⁵³ (see, e.g., the expression $4\hbar c/\lambda^3$ on p. 81 of Condon and Shortley¹⁵⁴).

We emphasize again that the values for minimum intensity or fluence needed to implement STIRAP are valid for radiation with transform limited spectral lines shape. When using the numbers given in Table I of the Appendix to scale with the help of Eq. (19) to longer interaction time than the given 10 ns, e.g., to the order of 10 μs , some caution is needed. For such long interaction times, the transformed limited spectral linewidth is of the order of 100 kHz, while cw lasers often have linewidths or several MHz. Thus, unless special efforts are made to stabilize the lasers,⁸⁹ phase fluctuation will be relevant, Eq. (17) applies, and the minimum intensity may be 2 or 3 orders of magnitude higher than calculated from Eq. (19).

On the other hand, when the values are scaled to much shorter interaction time, e.g., order of 10 ps, the field strength required for adiabatic evolution may be sufficiently high to

drive detrimental multi-photon transitions or induce Stark shifts which are of the order of, or larger than, the level spacing. In such cases, the transfer efficiency may be significantly reduced.

C. Collision dynamics

Coherent control of collision dynamics has been a key issue at many conferences for more than two decades. However, to the best of our knowledge, no experiments have hitherto explored the option to prepare a molecule (or an atom) prior to the collision in a coherent superposition state using STIRAP (cf. Ref. 66) and control the outcome of the collision through variation of the relative phase of the components of that superposition. Because the averaging over a large range of impact parameters during a collision process at thermal energy will most likely wash out any signature of phase control, such experiments are best done at ultracold temperatures, cf. Ospelkaus *et al.*¹⁵⁵ Also, a detailed theoretical analysis of an atomic collision process ($\text{Ne}^* + \text{Ar}$), aiming at the control of the branching between Penning ionization and associative ionization by Arago *et al.*,^{156,157} awaits experimental confirmation. Along the same lines, namely, the physics and chemistry of ultracold particles in the gas phase, Section IV A discussed a few experiments involving STIRAP, aiming at the formation of small molecules in their lowest energy state.

Photo-association of ultracold atoms has very recently emerged as a major field of experimental activities involving many research groups. One of the hopes is to find a means to form a molecular Bose-Einstein condensate, thereby giving BEC research a new dimension. A barrier preventing molecular BEC seems to be associated with collision or reaction processes which prevent reaching sufficiently low temperatures at sufficiently high particle densities.¹⁵⁸ A detailed analysis and understanding of such processes are therefore urgently needed.

D. Confined-matter waves

It was recognized some time ago that confined-matter waves can be efficiently transferred between spatially separated wells using STIRAP, a concept that has been named *Spatial adiabatic passage* (SAP)¹²³ or CTAP.¹²² The early work stimulated experiments that demonstrated light beams being transferred between waveguides, discussed in Sec. IV D. The challenge there is to provide sufficiently strong coupling between the separate wells. Very promising schemes have been suggested that propose realistic scenarios for the transfer of matter waves between suitable waveguides or spatially separated wells (see, e.g., Ref. 159). In that work, the authors state “spatial adiabatic passage allows one to control the tunneling process in a robust manner without requiring accurate control of the system parameters, and its properties.” That concept has also been applied to three-well interferometry of Bose-Einstein condensate, with the intent of allowing researchers to coherently split and recombine spatially separated parts of the condensate (cf. Rab *et al.*¹⁶⁰). Although experimental confirmation is still lacking, such experiments seem to be “around the corner.”

E. STIRAP in precision experiment

STIRAP has begun to play a role in precision experiments, e.g., those aiming at the determination of ever improving upper limits for the electric dipole-moment of the electron (eEDM). Results from such experiments, which measure extremely small shifts of the energies of quantum states, are of fundamental importance for testing extensions of the standard model of particle physics. Recent experiments¹⁶¹ use polar molecules having very strong intramolecular electric field, such as ThO, to enhance the sensitivity of level shifts to the electric eEDM. These experiments employ cryogenic molecular beams with the actual measurement done in an electronically excited metastable state $|m\rangle$ of the molecule. This state is efficiently populated by STIRAP from an initial state $|i\rangle$, in the electronic ground state, which is insensitive to external electric fields. In order to increase the flux of molecules in state $|i\rangle$ in the region where the measurement is done, the molecules are electrostatically focused, which requires population of a state $|e\rangle$ that is sensitive to external electric fields. STIRAP is also used to transfer molecules back and forth with high efficiency from state $|i\rangle$ to state $|e\rangle$ prior to transferring them into the state $|m\rangle$. Results from preliminary experiments along these lines are promising.¹⁶²

F. STIRAP in other solid-state systems

Solid-state systems seem, at first glance, to be a rather hostile environment for STIRAP-induced transfer because the required phase-stability is difficult to maintain. However, in addition to the work discussed in Sec. IV D, we also mention some interesting developments in other solid state systems. Already more than a decade ago, Hohenester *et al.*¹⁶³ analyzed coherent transfer of electrons between quantum dots. More recently, Falci *et al.*¹³³ proposed coherent population transfer in coupled superconducting nanocircuits (“artificial atoms”). Furthermore, dark states have been observed in low temperature optomechanical nanosystems.¹⁶⁴ One may therefore expect to see soon STIRAP-induced transfer between mechanical modes and light fields or even light-mediated transfer between quantum states of a nanomechanical system near its quantum mechanical ground state.¹⁶⁵

None of these concepts or proposals to implement STIRAP in a solid state system has yet been experimentally verified, but the results from theoretical analysis or preliminary experiments are sufficiently encouraging to expect experimental confirmation of some of the ideas. Successful implementation of coherent transfer scheme like STIRAP in solid state environment will be very important for, e.g., the implementation of quantum information schemes.

G. Summary

STIRAP, a technique for almost lossless transfer between quantum states, was developed for a specific use in the physical chemistry community, but the merits of the method were quickly recognized by others. In this article, we traced the breathtaking development which STIRAP has enjoyed since the original presentation of the concept in 1990.¹ This article

documented the wide range of application of STIRAP which went far beyond what was initially anticipated.

Here, we do also reemphasize some limitations. Being an adiabatic process relying on driving a system coherently, STIRAP requires radiation with (nearly) transform limited bandwidth. Also, before using laser pulses shorter than 1 ns, careful attention must be given to possibly detrimental multiphoton excitation or ionization processes that may prevent efficient population transfer to the target level. Furthermore, at high pulse, energy detrimental consequences because of Stark shifts of states are likely to prevent successful application of STIRAP. This is in particular true when considering STIRAP for larger molecules with their relatively small state-to-state transition dipole moments and closely spaced energy levels.⁶⁰ Indeed, so far, the most complex molecule for which STIRAP has been successfully implemented to be SO₂, by Halfmann and Bergmann³⁷ It is also true that unavoidable Stark shifts prevent using, e.g., two-photon transitions to reach high lying electronic states in the context of STIRAP (Refs. 45–47). Having put up these warning signs, we conclude with the message: with appropriate care, STIRAP has proven to be an amazingly powerful and versatile tool for manipulating quantum states and even classical systems.

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APPENDIX: CALCULATING STIRAP INTENSITY

For the transitions of usual interest in chemistry, the Rabi frequency is proportional to the electric field amplitude and the matrix element of a dipole-transition moment between distinguishable quantum states.^{22,26,166} The square of this Rabi frequency is proportional to the instantaneous intensity $I(t)$ and to a squared dipole-transition moment. This latter quantity factors into a dimensionless geometric factor^{22,166–168} $\mathcal{S}^{\text{geom}}$ (expressible as the square of a three-j symbol) that depends on magnetic quantum numbers M and the transition strength of Condon and Shortley¹⁵⁴ \mathcal{S} . For transitions of diatomic molecules, this latter quantity is, in turn, expressible as a Hönl-London (HL) factor^{17,150,151,169,170} \mathcal{S}^{rot} , depending on the rotational angular momentum J of the two states, and either an oscillator strength f or an Einstein A for a vibrational band.^{150–152} The relationship between spectroscopic quantities \mathcal{S} , f , and A is discussed in many references.^{151,154,166,171} Thus, the squared Rabi frequency is expressible as

$$|\Omega(t)|^2 = c_A I(t) \mathcal{S}^{\text{rot}} \mathcal{S}^{\text{geom}} \lambda^3 A_{v'v''}, \quad (\text{A1})$$

where c_A is a numerical factor, λ is the wavelength of the transition, and $A_{v'v''}$ is the band Einstein-A.^{147,150–152,172} The

TABLE I. Minimum intensity I^S or fluence F^S calculated from Eq. (19) needed to satisfy the adiabatic condition for STIRAP. Upper three lines: spectroscopic data for H_2 from Table 3 of Fantz and Wunderlich.¹⁴⁷ Middle three lines: spectroscopic data for Schumann-Runge band of O_2 from Table VII (a) of Laux and Kruger.¹⁷² From $v' = 10$, all vibrational levels at least in the range $0 < v'' < 18$ can be reached. Lower three lines: spectroscopic data for gamma band of NO from Table VI (a) of Laux and Kruger.¹⁷² The data on NO are consistent with experiments by Kuhn *et al.*³⁸ This agreement validates our approach to estimating fluence requirements.

H_2	$X^1\Sigma_g^+$	$B^1\Sigma_u^+$	λ (nm)	$A_{v',v''}$ (s^{-1})	T (ns)	I^S (mW/mm^2)	F^S ($\mu J/mm^2$)
P	$v'' = 0$	$v' = 4$	102	1.3×10^8	10	2.7×10^4	0.27
S	$v'' = 8$	$v' = 4$	146	8.4×10^7	10	1.4×10^4	0.14
O_2	$X^3\Sigma_g^-$	$B^3\Sigma_u^-$	λ (nm)	$A_{v',v''}$ (s^{-1})	T (ns)	I^S (mW/mm^2)	F^S ($\mu J/mm^2$)
P	$v'' = 0$	$v' = 10$	182	3.0×10^4	10	2.0×10^7	2.0×10^2
S	$v'' = 15$	$v' = 10$	295	3.2×10^5	10	4.5×10^5	4.5
NO	$X^2\Pi_r$	$A^2\Sigma^+$	λ (nm)	$A_{v',v''}$ (s^{-1})	T (ns)	I^S (mW/mm^2)	F^S ($\mu J/mm^2$)
P	$v'' = 0$	$v' = 0$	226	9.5×10^5	3	3.7×10^5	11
S	$v'' = 6$	$v' = 0$	300	7.9×10^5	3	1.9×10^7	59

dependence on angular-momentum quantum numbers J and M occurs in the factor $S^{\text{rot}}S^{\text{geom}} \equiv S$.

We invert formula (A1) to obtain the peak intensity I^{max} as a function of peak Rabi frequency Ω^{max} for each of the two pulses. Using estimates of those peak Rabi frequencies based on the requirement of adiabaticity¹⁹ $\Omega^{\text{max}}T \geq 10$ or $\Omega^{\text{max}} \geq 10/T$, we obtain the minimum peak intensity, I^S , needed to accomplish STIRAP. Based on the approximation discussed above, we estimate the minimum intensity needed to satisfy the adiabaticity condition for STIRAP from the formula

$$I^S = \frac{4}{3} \frac{\hbar c \pi^2}{\lambda^3 S A_{v',v''}} \left(\frac{10}{T} \right)^2. \quad (\text{A2})$$

Generally, observations of population dynamics will sum over transitions that start from different magnetic sublevels and hence with different geometric factors of the Rabi frequency, as discussed in Sec. II F. As pointed out by Gaubatz *et al.*,¹ for successful STIRAP of all magnetic sublevels, it is necessary that the adiabaticity criterion be satisfied for the transition with the smallest dipole-transition moment.

To estimate S for the present purpose, we reason as follows. The Einstein coefficient $A_{v'',v'}$ for diatomic molecules gives the sum of the decay rates of a quantum state (j', m') in the vibrational level v' to all accessible states (j'', m'') in the lower lying vibrational level v'' . Optical selection rules restrict transition to $|j' - j''| = 1$ or 0 and $|m' - m''| = 1$ or 0 . Thus, in the general case, $A_{v'',v'}$ is the sum of the decay rates into 9 channels. The individual rates for transitions between (j', m') and (j'', m'') depend through S on the related HL factors S^{rot} and geometric factors S^{geom} , which can be evaluated when the structure of the electronic states is known and specific transitions are chosen. For the purpose of estimating I^S , we take these decay rates to be equal. Therefore, as an approximation suitable for this estimate, we take the transition rate for (v', j', m') to (v'', j'', m'') to be $A_{v'',v'}/9$, i.e., we take in Eq. (A2) the value $S = 1/9$. In doing so, we disregard the fact that in some cases, $|j' - j''| = 0$ is not allowed and we have only 6 decay channels, or even fewer if not all of the transitions $|m' - m''| = 1$ or 0 are possible. In such a case, the consequence of assuming 9 decay channels is that I^S comes out higher unless

the factor of 9 is replaced by the number of actually available decay channels. With these approximations, we obtain, from data in the literature,^{147,172} the results shown in Table I.

We note that the $B^3\Sigma_u^-$ state of O_2 predissociates because its potential curve is crossed by those of repulsive states. However, when properly implemented, the intermediate state is not populated and thus the predissociation is not detrimental for the transfer process.

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