Stimulated Raman adiabatic passage with pulsed lasers: High resolution ion dip spectroscopy of polyatomic molecules

R. Sussmann, R. Neuhauser, and H. J. Neusser
Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany

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The interaction of two narrow band ($\Delta\nu$<100 MHz) UV light pulses of different intensity with a molecular three-level system is investigated experimentally. The laser frequencies are tuned to an up (pump) and a down (dump) transition sharing a common excited rovibronic S_1 level whose population is probed by a transition to the ionization continuum and ion detection. The time sequence of the two pulses results either in a lambda type coherent stimulated Raman adiabatic passage or a stimulated emission pumping (SEP) process. When the first case is realized by a 6.4 ns delay of the low intensity pump laser from the high intensity dump laser pulse, a fourfold increase of the depth of the ion dips compared to the SEP experiment is observed. This is in line with numerical calculations of the level populations using a density matrix formalism including coherent effects. Rotationally resolved ion dip spectra of the 6_2 state of benzene are presented and demonstrate the high sensitivity of the coherent excitation process of this work for ion dip spectroscopy.

I. INTRODUCTION

When intense narrow band laser light interacts with atomic or molecular systems, coherent effects have to be taken into account.[1] Typically, coherent effects become relevant when the Rabi frequency is larger than the rate of the intramolecular or radiative relaxation process. An effect which is supposed to be of practical importance is the complete population transfer from an initial state to a final state in a three level system without population in the intermediate state by adiabatic passage either in a ladder[2–5] or in a lambda type system.[6,7] For the latter case, stimulated Raman adiabatic passage (the acronym STIRAP) is used. Recent STIRAP experiments with two partially overlapping cw laser beams crossing a molecular beam support these model predictions.[8] The adiabatic passage was achieved by the transfer of Na_2 molecules in the molecular beam expansion from one laser beam to the other. The jet expanded molecules (Na_2) interacted first with the dump laser beam and then entered the pump laser beam.

The excitation scheme of a lambda type Raman transition includes a laser frequency in resonance with the transition from a ground initial state to an excited state and a second laser frequency in resonance with a transition from the excited state to a lower final state. This is identical with the excitation scheme in stimulated emission pumping (SEP) experiments (with incoherent laser light) leading, e.g., to the excitation of highly vibrational excited levels in a variety of molecules and small complexes.[9] In SEP experiments, the first laser is the pump laser and the second one is the dump laser. To simplify, we will use this nomenclature also in the coherent experiments of this work, though it is not correct in the latter case since the time sequence of the two excitation processes is inverted. In a SEP experiment, the dump transition is stimulated after pumping the upper level, thus transferring population from the excited level to the final ground level. In this way, a population of the final state of 25% can be obtained. From the practical point of view, this means that the depth of the dips obtained in a SEP experiment cannot exceed 50%. It has been proposed for STIRAP experiments that the population can be completely transfered to the final level without any population captured in the excited state leading to 100% dips.[10]

For weak UV transitions and for time dependent investigations, an experiment with pulsed lasers is desirable. In coherent excitation processes, phase fluctuations of the two laser pulses should be as small as possible, which is best achieved for Fourier transform limited pulses, difficult to produce by a pulsed oscillator. These strict requirements have prevented the experimental realization of STIRAP with pulsed lasers for a long time.[11]

In this work, we present the demonstration of a coherent adiabatic following process using narrow band nanosecond laser pulses which is related to STIRAP experiments. We address the question whether the coherent adiabatic process can lead to an improvement of ion dip spectra usually obtained in SEP experiments. For this purpose, a special pulse sequence with a weak delayed pump pulse and a stronger dump pulse is used which guarantees that there is no population trapped in the intermediate state of the lambda type transition. In contrast to a STIRAP experiment,[6,7] this is not achieved by an efficient population transfer to the final state, but rather by a transfer of the population back to the initial state. This will be called "modified STIRAP" configuration throughout the text, taking into account the similarity of both processes in a lambda type three level system. Modified STIRAP includes two delayed light pulses of different intensity. The broad strong dump pulse is followed by a less intense narrower pump pulse. The delay of the pump pulse is chosen so that the weak pump pulse is within the falling edge of the stronger dump pulse. Numerical estimates predict a depopulation of the excited level when the dump laser is tuned to resonance with the transition frequency from the excited to the final state because no transient population in the intermediate level results in the modified STIRAP configuration. The experimental bases for this experiment are two indepen-

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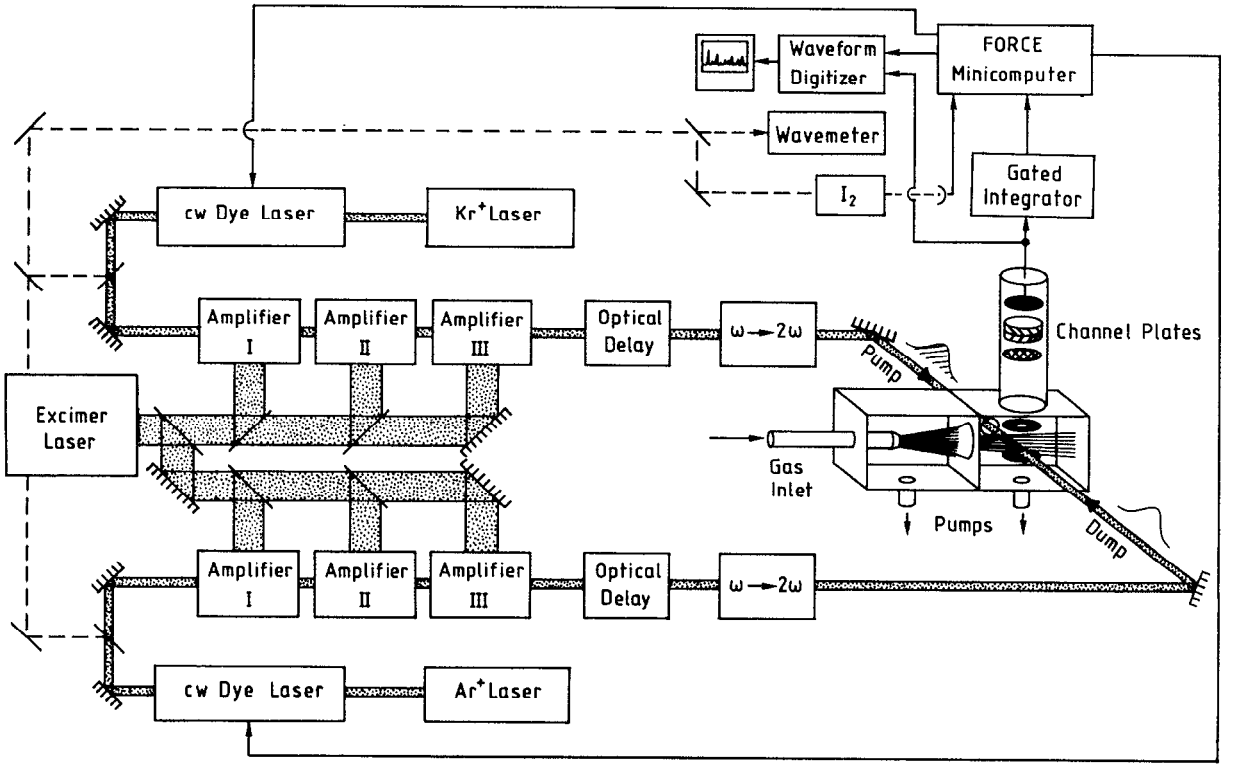

FIG. 1. The experimental setup for recording of rotationally resolved ion dip spectra of single rovibronic states of benzene. A spectral resolution of the pump and the dump lasers of $\Delta\nu_{UV}<100$ MHz (FWHM) is obtained by pulsed amplification of the cw light of two single-mode dye lasers and subsequent frequency doubling. The counterpropagating pump and dump laser beams are crossed with the molecular beam produced in a skimmed supersonic jet.

dently tunable cw ring lasers, the light of which is pulsed amplified in two amplifier stages. The nearly Fourier transform limited pulses interact with the $6^1(J'_{K'}=4_4, l'=-1)$, $S_1\leftarrow S_0$, $0_0(J''_{K''}=3_3)$ transition (pump) and the $6^1(J'_{K'}=4_4, l'=-1)\rightarrow 6_2(\Delta J=0,\pm1, \Delta K=\pm1)$ transition (dump) of benzene molecules in a cooled supersonic jet. Here J and K are the rotational quantum numbers of a symmetric top; the vibrational angular momentum with quantum number l causes a splitting of each rotational state in the degenerate 6^1 and 6_2 vibronic states due to Coriolis coupling.[12] The Doppler width is reduced to 40 MHz using a skimmer and individual rovibronic transitions are resolved in the pump and the dump transitions. Unlike the SEP experiment in our modified STIRAP experiment, the pump laser pulse is delayed by 6.4 ns from the dump laser pulse leading to a complete overlap of both pulses. The population of the excited $6^1(J'_{K'}=4_4, l'=-1)$ level is monitored by an absorption step to the ionization continuum induced by the absorption of a second photon mainly from the dump laser and the resulting ions are detected in a time-of-flight (TOF) mass spectrometer. The observed ion dips have a depth of 95%, which exceeds the depth of 25% achieved in the SEP experiment.

II. EXPERIMENT

The scheme of the experimental setup is shown in Fig. 1. Pump and dump laser pulses are provided by two pulsed amplified cw lasers. The cw ring laser (Coherent 699/21) yielding the pump pulse is operated at $\lambda=518$ nm with coumarin 102 dye. It is pumped by the multiline violet output of a Kr^+ laser (Coherent Innova 200). The cw light with a frequency width of 2 MHz is amplified in a three stage amplifier system[13,14] yielding nearly Fourier transform limited light pulses with a pulse energy of 400 μJ, a width of 10 ns [full width at half-maximum (FWHM)] and a frequency width of 100 MHz (FWHM) after frequency doubling in a BBO crystal. The cw ring laser providing the dump pulse is pumped by the 514.5 nm line of an Ar^+ laser (Spectra Physics 171) and operated at $\lambda=534.9$ nm with rhodamine 110 dye. The pulse energy after amplification and frequency doubling in a KDP crystal is 1 mJ for a pulse width of 20 ns (FWHM) and a frequency width of 60 MHz (FWHM). Both amplifier stages are pumped by the 300 mJ pulses ($\lambda=308$ nm) of an excimer laser (Lambda Physik EMG 201 MSC). Pump and dump laser beams are focused down to 0.5 mm. The pump laser is attenuated by a factor of 50 in the SEP as well as in the modified STIRAP experiment to avoid absorption of a second photon from this laser resulting in an ionization of the molecule. For the modified STIRAP experiment, the pump pulse is delayed by 6.4 ns from the dump pulse, whereas in the SEP experiment, the dump pulse is delayed by 17.8 ns from the pump pulse. This is possible without loss of peak power and beam quality in a special multipass reflection cell.[15] Both counterpropagating narrow band light pulses interact with benzene molecules in the center of a cooled supersonic beam expanded from a reservoir with 1% benzene seeded in Ar at a backing pressure of 2 bar through a nozzle with a 300 μm diameter orifice.[16] Counter-

propagating laser beams result in Doppler broadened Raman transitions as pointed out in Refs. 17 and 18. A conical skimmer (1.5 mm diameter) collimates the beam and reduces the residual Doppler width below the laser linewidth. Thus there is no substantial contribution from Doppler broadening to the measured linewidth. The absorption of a second dump laser photon from the excited 6^1 state results in an ionization of the molecule. For the inverted delay chosen in our modified STIRAP configuration, sufficient intensity of the (first) dump laser is present when the pump laser pulse arrives. In this way, the population in the intermediate state is probed. The molecular ions are mass separated in a time-of-flight mass spectrometer and detected with multichannel plates. The recorded spectra were not normalized to the UV power of the lasers. There was no signal averaging over several pulses. Only a Gaussian filter of ten experimental points (FWHM) was used in the displayed spectra of Figs. 3 and 4. Scanning the pump laser from 38 604 to 38 608 cm^{-1} for a fixed nonresonant frequency of the (ionizing) dump laser and integrating the ion signal at mass 78 u yields a rotationally resolved spectrum of the 6_0^1 band of benzene.[16] For the SEP and the modified STIRAP experiments, the pump laser frequency is then kept constant on top of a single selected rotational line, while the dump laser is scanned around the expected transition frequencies down to a selected rovibrational state in the S_0 electronic ground state. The time sequence of the pulses depends on the type of the experiment, either SEP or modified STIRAP. The relative frequency of the dump laser is measured with a 150 MHz free spectral range interferometer and the absolute frequency is calibrated by the simultaneously measured fluorescence spectrum of I_2 vapor.

III. EXPERIMENTAL RESULTS

A. Stimulated emission pumping (SEP)

In this experiment, the dump laser pulse is delayed from the pump laser pulse. According to the excitation scheme in Fig. 2, the absorption of a pump laser photon ($h\nu_1$) leads to the population of the excited state which is depleted by stimulated emission when the dump laser frequency ($h\nu_2$) is in resonance with a transition down to a rovibrational level in the S_0 ground state. The lifetime of the 6^1 state of 79 ns (Ref. 19) is much longer than the delay of the dump pulse, i.e., there is no loss of population after the delay time of 17.8 ns through a nonradiative deactivation of this state. The population of the excited state is probed by the absorption of an additional photon of the dump laser ($h\nu_2$) leading to the ionization of the molecule. The ion current at mass 78 u is measured as a function of the frequency of the dump laser.

In Fig. 3, the result is shown when the pump laser frequency is fixed on top of the $J'_{K'}=4_4$, $\Delta J=\Delta K=+1$ line in the 6_0^1 band of benzene and the dump laser scanned from 37 386 to 37 391 cm^{-1}. The spectrum shown in Fig. 3 is not normalized to the UV power of both lasers. The relative frequency is given in gigahertz. Four sharp dips are observed at -55, -45, 0, and 45 GHz, respectively. These dips are caused by transitions with $\Delta J=0, \pm 1$ and $\Delta K=\pm 1$ from the excited $6^1(J'_{K'}=4_4, l'=-1)$ to the $6_2(J''_{K''}=5_5, 5_3, 4_3, 3_3)$ states in the electronic ground state S_0. The absolute wave

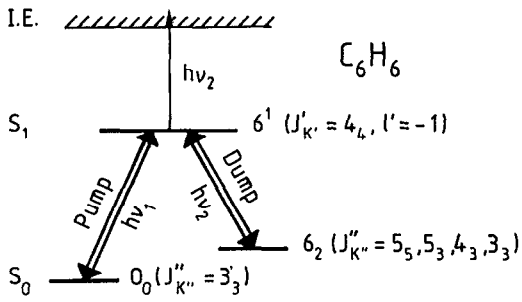

FIG. 2. The excitation scheme for the stimulated emission pumping (SEP) and the stimulated Raman adiabatic passage experiment (modified STIRAP) of this work. Single rovibrational levels in the ground S_0 and the excited S_1 electronic states of benzene are indicated. J and K are the rotational quantum numbers and l describes the vibrational angular momentum of the degenerate 6^1 state with one quantum of the ν_6 vibration excited in the S_1 electronic state. The terms pump ($h\nu_1$) and dump ($h\nu_2$) laser of a SEP experiment are also used for the modified STIRAP experiment. Note the differing time sequence of the pump and the dump pulses in the SEP and the modified STIRAP experiment described in the text and the insets of Figs. 3 and 4.

number of the $J'_{K'}=4_4, l'=-1 \rightarrow J''_{K''}=4_3, l''=0$ transition is 37 388.84(1) cm^{-1}, which corresponds to an excess energy of 1219.85(1) cm^{-1} of the $6_2(J''_{K''}=4_3, l''=0)$ state above the zero point level. The same transitions, however, at much lower resolution, were observed in our previous work.[20] There the selection rules and intensities are discussed in more detail. From the line positions, the rotational constants of the 6_2 ground state can be deduced with high accuracy. This is the subject of a subsequent work.[21] The decrease of the slope in the baseline at the 100% level is produced by a slight frequency drift of the pump laser from the top of the line during the 5 min scanning time of the dump laser. The observed dips have a width of 300–500 MHz, which is larger than the frequency width of the dump laser. This broadening is probably caused by a saturation of the dump transition. The depth of the peaks is about 25%. This is the best result obtained for optimized experimental conditions.

B. Stimulated Raman adiabatic passage (modified STIRAP)

As described in the Introduction, coherent effects are expected for the narrow bandwidth of our two laser pulses. The preconditions for a modified STIRAP experiment are met by a 6.4 ns delay of the pump pulse from the dump pulse. For this delay, a temporal overlap of both laser pulses exists which is discussed in Sec. IV. The frequency of the delayed pump laser pulse is tuned to the maximum of the transition leading to the $J'_{K'}=4_4, l'=-1$ excited state and the frequency of the dump laser pulse is scanned over the same frequency range as shown in Fig. 3. Optimum experimental conditions were obtained for a pulse energy of 1 mJ of the dump laser (corresponding to an estimated Rabi frequency at the peak maximum of $\Omega_2=14\times10^{10}\ s^{-1}$ as derived below) and 10 μJ of the pump laser (corresponding to $\Omega_1=2\times10^{10}\ s^{-1}$), respectively. The low power of the pump laser reduces the ionization signal background produced by

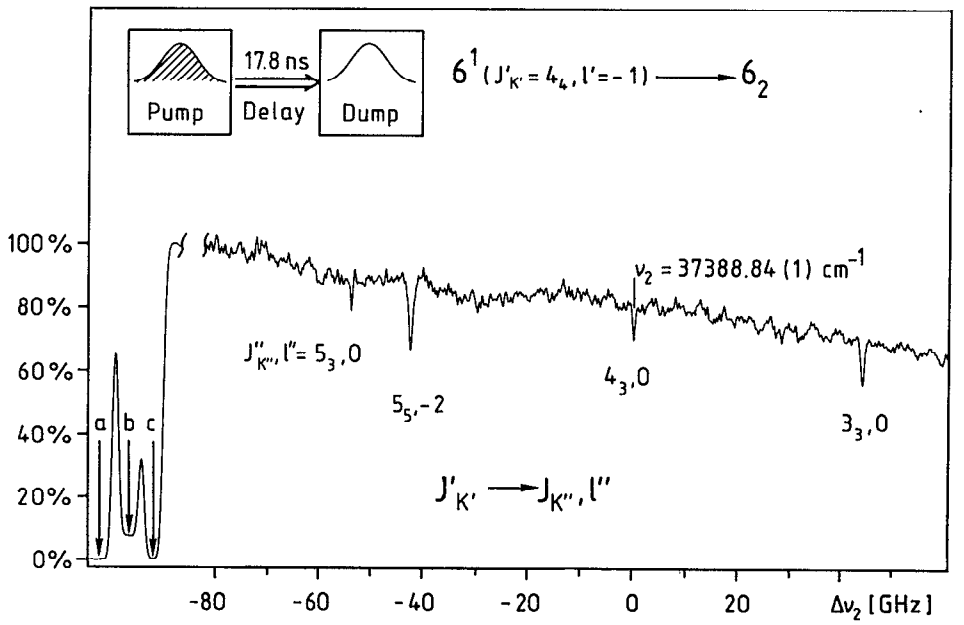

FIG. 3. The ion dip signal after selective excitation of the $J'_{K'} = 4_4$, $l' = -1$ rotational state of the 6^1 vibronic state of C_6H_6 as a function of the dump laser frequency. For the indicated line, the absolute frequency position is given. The indicated delay of the dump laser pulse leads to a SEP type spectrum. The displayed spectrum is not normalized to the UV power of the lasers. In the left part of the figure, the zero signal calibration is shown (a) both lasers blocked; (b) dump laser blocked; and (c) pump laser blocked.

the absorption of two photons from this laser beam. The resulting ion signal is shown in Fig. 4 as a function of the dump laser frequency. Again four dips are observed whose peak positions agree with the peak positions in Fig. 3 within the experimental error of 100 MHz. There are, however, two striking differences in Figs. 3 and Fig. 4. (i) The coherent process leads to deeper dips in Fig. 4. Taking the zero signal level {both lasers blocked [Fig. 4(a)]} as reference, the strongest dip shows a 95% depth. Taking the small background signal of the pump laser alone {dump laser blocked, [Fig. 4(b)]} as reference, the strongest dip is deeper than 99%. (ii) The widths and the shape of the SEP and modified STIRAP dips differ strongly. Though the width (FWHM) of the deepest modified STIRAP dip is larger by a factor of 4 than the

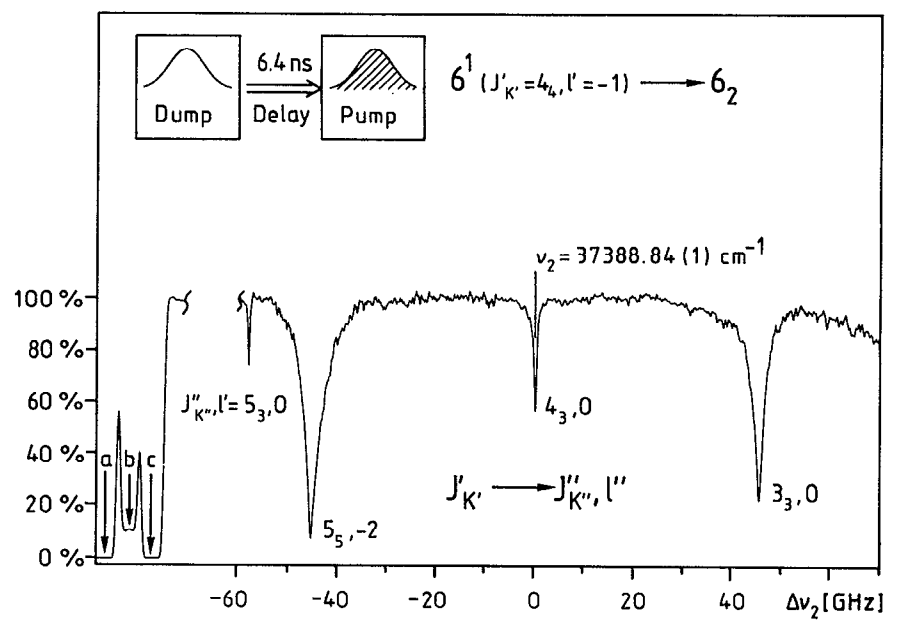

FIG. 4. The ion dip spectrum of the same spectral region as shown in Fig. 3 with the indicated time sequence of the lasers leading to a modified STIRAP process (pump laser delayed by 6.4 ns). As in Fig. 3, no UV power normalizing or signal averaging procedure was used. In the left part of the figure, the zero signal calibration is shown (a) both lasers blocked; (b) dump laser blocked; and (c) pump laser blocked.

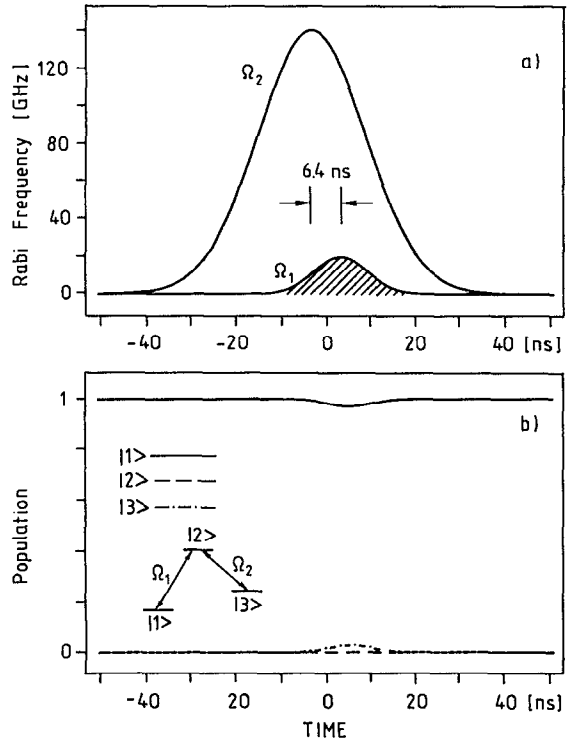

FIG. 5. (a) Time evolution of the Rabi frequencies Ω_1 and Ω_2 for the time sequence of the dump and pump pulses in our modified STIRAP configuration. (b) Population of the levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ (see the inset) as a function of time calculated numerically from the density matrix equations in the rotating wave approximation for the Rabi frequencies in (a). A small amount of transient population (≈2%) is transfered from level $|1\rangle$ to level $|3\rangle$ and then transfered back to level $|1\rangle$. No transient population in level $|2\rangle$ is displayed.

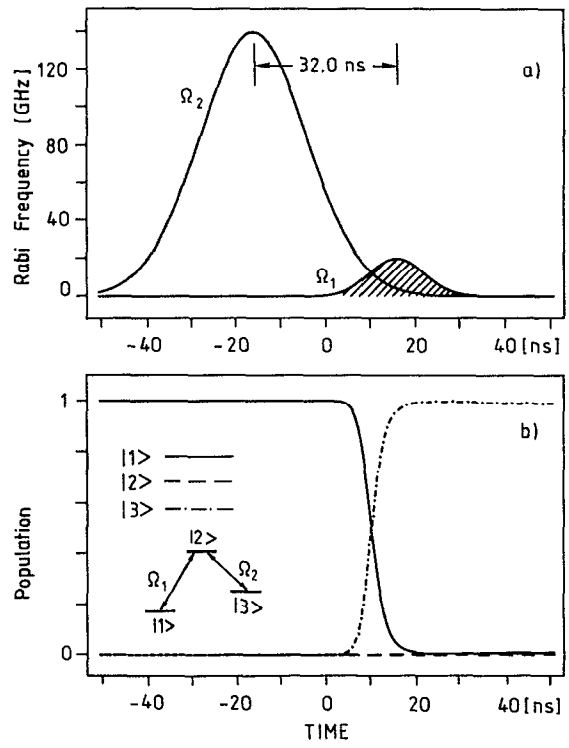

FIG. 6. (a) Time evolution of the Rabi frequencies Ω_1 and Ω_2 for a conventional STIRAP configuration (Ref. 8) with a longer delay of the pump pulse of 32 ns. (b) Population of the levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ as a function of time numerically calculated from the density matrix equations in the rotating wave approximation for the Rabi frequencies in (a). Population is completely transfered from level $|1\rangle$ to level $|3\rangle$. No transient population in level $|2\rangle$ is displayed.

SEP dips, the sharpness of the peak maximum is comparable in both cases. Smaller dips in the modified STIRAP experiment are narrower [300 MHz (FWHM)]. This is important for high accuracy spectroscopic investigations of the peak positions yielding rotational constants, etc.

IV. DISCUSSION

The 95% depth of the ion dips of Fig. 4 demonstrates clearly that we observe a coherent adiabatic process in our experiment. An ion dip with a depth of 95% means that during the probing time, only 5% of the population is transfered to the excited state. In the view of a conventional STIRAP configuration,[8] the remaining 95% would be transfered directly from the initial to the final state. Here we would like to show that the different pulse intensities and the delay used in our modified STIRAP configuration lead to a direct population transfer from the initial to the final state followed by a prompt reverse transfer back to the initial state.

For this, we estimate the Rabi frequency $\Omega_1=\mu_1 E_1/\hbar$ for the pump transition $6^1(J'_{K'}=4_4,l'=-1)$, $S_1\leftarrow S_0$, $0_0(J''_{K''}=3_3)$ excited in our experiments with a pulse energy of 10 μJ, a pulse length of 10 ns, and a resulting light field of $E_1=1.4\times10^6$ V cm^{-1}. An upper value for the transition dipole moment matrix element μ_1 is deduced from the radiative lifetime τ_r of the 6^1 state. This represents an upper limit since transitions to other vibrational ground states must be taken into account as observed in the spontaneous emission spectrum from the 6^1 level.[22] τ_r is related to the fluorescence quantum yield Q_F and the fluorescence lifetime τ_F by

$$Q_F=(\tau_r)^{-1}/(\tau_F)^{-1} \quad \text{and} \quad (\tau_F)^{-1}=(\tau_r)^{-1}+(\tau_{nr})^{-1}, \tag{1}$$

where τ_{nr} is the lifetime due to the nonradiative decay of the excited level. From the experimental values $Q_F=0.24$ (Refs. 19 and 23) and $\tau_F=79$ ns,[19] we obtain from Eq. (1) $\tau_r=370$ ns. Assuming that the radiative depopulation of the excited 6^1 state proceeds through spontaneous emission to a single final rovibrational state, we use

$$\mu=3.08\times10^{-11}(\tau_r\nu^3)^{-1/2} \quad \text{(SI units)}. \tag{2}$$

For $\nu_1=38\,606$ cm^{-1} and $\tau_r=370$ ns, we find $\mu_1=1.28\times10^{-30}$ Cm. With $\mu_1=1.28\times10^{-30}$ Cm and $E_1=1.4\times10^6$ V cm^{-1}, we find $\Omega_1=2\times10^{10}$ s^{-1}. We use $\Omega_2=14\times10^{10}$ s^{-1} for the dump transition with the stronger laser pulse ($E_2=9.8\times10^6$ V cm^{-1}).

We performed numerical calculations solving the density matrix model equations[24] for a three level system with different Rabi frequencies for the pump and the dump transition, assuming no phase fluctuations in our laser pulses (i.e., exactly Fourier transform limited laser pulses) and neglecting the ionization step. In Figs. 5 and 6, the calculated results for the population of the initial level, the excited level, and

the final level are shown for two pulse delays as a function of time. For illustration of the time delay, the Rabi frequency of the two pulses is depicted as a function of time in Figs. 5(a) and 6(a). The peak values are identical with the values for Ω_1 and Ω_2 given above. For the configuration of Fig. 5(a), the delay of the peak maxima is 6.4 ns and corresponds to the experimental value. A longer delay of 32 ns leads to the curves in Fig. 6(a) and represents a pulse configuration which is closer to the STIRAP situation described in Ref. 8 for two pulses with equal intensity. It is interesting to compare the numerical results for the level populations obtained in both cases (Figs. 5 and 6). For the pulse configuration of our experiment it can be seen from Fig. 5 that $\approx 2\%$ population of the ground state level ($|1\rangle$) is transfered directly to the final state ($|3\rangle$) to be subsequently transfered back to the initial state during the pulse overlap without any noticeable population in the excited level ($|2\rangle$), even though the pump laser frequency is in resonance with the transition frequency from the ground state to the excited state. This is not the situation proposed in Ref. 8, but from the results in Fig. 5(b), it is concluded that no population in the excited level can be monitored when the dump laser frequency is in resonance with the transition frequency from the excited to the final level, thus leading to a 100% ion dip. The 95% observed in our experiment (Fig. 4) is close to this ideal value.

For the longer delay of the pump pulse (Fig. 6), an efficient population transfer from the initial to the final level is theoretically found as proposed in Ref. 8. Experimentally, for a longer delay of 17.7 ns, a noisy baseline at the 100% level was observed, due to the lower intensity of the dump laser during the pulse overlap leading to less efficient ionization, when the dump laser frequency is out of resonance.

The modified STIRAP method presented in this work is particularly valuable for sensitive ion dip spectroscopy. As shown above, it leads to a fourfold increase of the depth of the ion dips when compared to incoherent SEP experiments with a strongly increased signal to noise ratio. On the other hand, the modified STIRAP technique is not useful when the dynamics of the final level is investigated since this state is not populated. This is the purpose of many SEP experiments.[9]

V. SUMMARY AND CONCLUSION

In conclusion, in this work stimulated Raman adiabatic processes with pulsed narrow band lasers are observed. It is demonstrated for the first time that this is a valuable new method for ion dip spectroscopy. Coherent adiabatic processes with a moderately delayed low intensity pump pulse and a totally overlapping stronger dump pulse lead to deep ion dips. The configuration of this stimulated Raman adiabatic process is different from the STIRAP process proposed in the literature for an efficient population transfer from a ground state to a final state. We realized the coherent adiabatic process for the example of a polyatomic molecule, benzene, and observed ion dips with a depth of 95%. For practical purposes, it is important that the ion dips obtained by coherent adiabatic processes are deeper than in the SEP spectrum, while providing the same spectral information. Future applications of this technique will include sensitive high resolution spectroscopy of the ground state of clusters.

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