Degenerate and two-color resonant four-wave mixing of C_2^- in a molecular beam environment

Marek Tulej,[†] Gregor Knopp, Thomas Gerber and Peter P. Radi*

In this paper, we demonstrate that degenerate and two-color resonant four-wave mixing spectroscopy is applicable for the sensitive and selective characterization of negative ions in a molecular beam environment. Results are shown for C_2^-, which is produced by discharging a mixture of acetylene and argon prior to supersonic expansion. Substantial signal-to-noise ratios of ≈ 150 show that the method is generally applicable for high-resolution optical double-resonance spectroscopy of negative ions. A detection sensitivity for C_2^- of $\approx 10^7$ ions/cm^3 is estimated. Copyright © 2010 John Wiley & Sons, Ltd.

Introduction

Molecular anions are relevant in astronomy,[1] in the upper atmosphere,[2] in laboratory discharges,[3] and in combustion. Actually, anions are present in most combustion systems and are assumed to play an important role in reactions forming pollutants such as soot[4–6] and aerosols from aircraft engines.[7] In a recent work, Warnatz and coworkers[8] included negative ions in the chemical reaction mechanism of the modeling of a fuel-lean methane–oxygen flame and emphasized the relevance of anions. In particular, detailed reaction mechanisms involving negatively charged species are required for the calculations of the electrical conductivity, which is essential for technical applications.

In spite of their importance, only a few anions have been spectroscopically characterized. It is difficult to generate anions in sufficient abundance for spectroscopic studies. Negative ions are far less abundant in most of the experimental environments than neutrals or cations.[9] Often, anions are generated in a plasma where numerous species coexist whose spectra may overlap. Therefore, highly sensitive methods are required that are suitable for low-density environments. In addition, the identification and characterization of specific ions demand techniques exhibiting a substantial selectivity in order to disentangle the spectral features. An additional challenge for spectroscopic investigations of anions is the binding energy of the excess electrons, which is usually small such that excited electronic states cannot exist.

Nevertheless, rotationally resolved electronic spectroscopy of valence- or dipole-bound states has been achieved for a number of anions. The most prominent anion in this respect is C_2^-. Its electronic spectroscopy has been studied extensively.[10–19] Rotationally resolved electronic spectra have also been obtained for CH_2CN^-,[20] H_2CCC^-,[21,22] C_4H^-,[23] C_4^-,[24] C_3^-,[25] CH_2CHO^-,[26,27] CH_2COF^-,[28] FeO^-,[29] and CH_2CN^-.[20,30] Recently, $SCCS^-$ has been measured by laser-induced fluorescence in a discharged supersonic jet.[31] In the latter work, fluorescence depletion spectroscopy – a variant of optical–optical double resonance spectroscopy – is employed in addition, to investigate spectral regions where the fluorescence quantum yield is very low due to

a fast nonradiative process. In fact, apart from the detection of transitions that exhibit low fluorescence yield, double-resonant spectroscopic techniques are advantageous to disentangle complex spectra of polyatomic molecules and to increase the selectivity in regions where spectra of different species overlap. However, the main inconvenience of fluorescence depletion spectroscopy is that the signal of interest is detected as a weak depletion superimposed upon an often fluctuating fluorescence background.

In the following, an alternative background-free and highly sensitive method that features double-resonance capabilities is applied to an anion. Degenerate four-wave mixing (DFWM) and two-color resonant four-wave mixing (TC-RFWM) are nonlinear spectroscopic tools exhibiting high signal-to-noise ratios (SNRs) resulting from a fully resonant process. The coherent, laser-like signal beam ensures collection of the entire signal rather than a small fraction as compared to an incoherent process like Raman scattering or laser-induced fluorescence. In addition to the high collection efficiency, a coherent signal beam allows the rejection of stray light by remote probing. The resulting high sensitivity renders the techniques applicable to species that are present in low concentrations. This property has been successfully exploited for DFWM measurements of trace species in low-pressure cells, flames, spark-ignition engines, and molecular beams.[32–52]

The nonlinear methods are often complementary to the more conventional linear spectroscopic techniques and offer sometimes additional capabilities.[51,53] Because four-wave mixing is based on absorption, the signal intensity is insensitive to the lifetime of the upper level.[54] As a consequence, the large and

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* Correspondence to: Peter P. Radi, General Energy Research Department, Paul Scherrer Institute, CH-5232 Villigen, Switzerland. E-mail: peter.radi@psi.ch

† Present Address: Institute of Physics, Planetology and Space Research, University of Bern, Sidlerstr. 5, CH-3012 Bern, Switzerland.

General Energy Research Department, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

important category of molecules exhibiting nonfluorescing[55] or predissociative states are accessible.[56–60] A further advantage has been demonstrated recently by Maier's group in Basel.[61] The high temporal resolution of four-wave mixing spectroscopy on the order of a few nanoseconds is sufficient to discriminate between individual species in a discharged molecular beam on the basis of their different formation times. This is in contrast to cavity ring-down spectroscopy,[62] a process occurring on a time scale that is at least three orders of magnitudes longer.

An additional benefit is obtained by using two distinct input frequencies for TC-RFWM. A signal is obtained exclusively when both frequencies interact with distinct molecular transitions that share a common level. As for all double-resonant techniques, the enhanced selectivity by intermediate level labeling is advantageous for the simplification of spectrally congested regions. Furthermore, rotational characterization of high-lying vibrational states on the ground potential energy surface is feasible by the stimulated emission pumping (SEP) variant of TC-RFWM.[48,63]

In spite of the quadratic dependence of the four-wave mixing signal on number density,[64] we have shown recently that DFWM and TC-RFWM techniques are sufficiently sensitive for the detection and characterization of low-abundance molecules. Substantial SNRs have been obtained for transient species in a molecular beam that are generated in a discharge assembly prior to supersonic expansion. For example, an SNR of up to 50 000 for the rotationally resolved $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ transition of C_3 has been obtained by discharging an acetylene/argon mixture.[53] The latter experiment has been performed by using a cylindrical nozzle assembly. By introducing a discharge assembly designed to provide a two-dimensional slit expansion that increases the interaction volume of the four-wave mixing beams with the molecular beam, a further increase in sensitivity could be achieved. In fact, experiments on the C_2 and HC_4S radicals resulted in high SNRs and a DFWM sensitivity among the highest was achieved.[65] In the following, we take four-wave mixing spectroscopy one step further and demonstrate its excellent sensitivity by applying the method to an anion, C_2^-, emerging from a supersonic slit discharge.[59]

Experimental

We briefly outline the DFWM and TC-RFWM experiments in our laboratory in the following; a detailed description of the molecular beam apparatus[53] and the slit-jet discharge source[65] has been published elsewhere.

The carbon dimer anion and other neutral and charged hydrocarbon species are generated by using a pulsed slit-jet discharge source based on a design by Linnartz.[66] The source assembly contains a set of electrically isolated steel electrodes mounted on the multichannel body by glass ceramic spacers. The multichannel body consists of several ducts of different diameters and establishes an even flow for a planar, two-dimensional expansion through a long and narrow slit which offers an essentially Doppler-free environment. The high density at the nozzle exit promotes equilibration of the translational and internal degrees of freedom of the radicals. In addition, the two-dimensional geometry is optimally adapted to the four-wave mixing experiment setup in a BOXCARS configuration.[67] The quadratic dependence of the technique on path length and number density, and taking into account the ability of precise

phase-matching over distances limited only by the coherence properties of the laser and the dimensions of the sample, yields a substantial enhancement of the signals. In fact, it has been estimated that over two orders of magnitude enhancement should be realized by replacing the pinhole with a planar slit assembly.[68]

A typical experimental procedure for the production of C_2^- starts with a trigger to the solenoid valve to expand $\approx5\%$ of acetylene diluted in argon. At a variable time after the valve opening, a well-defined high-voltage pulse of $\approx900\,V$ and adjustable duration (Velonex 345) is applied to the discharge electrodes. By changing the polarity of the discharge, the direction of the electrons to either co- or counter-propagation with respect to the molecular beam can be chosen. For C_2^- in particular, a polarity is favorable that yields counter-propagating electrons. A precise optimization of the voltage, trigger delay, trigger duration, and polarity yields an intense and remarkably stable molecular beam. The molecular beam propagates into the vacuum chamber pumped by a 1400 l/s turbo pump. During operation, the source chamber is at a typical pressure of $\approx10^{-2}\,Pa$. The application of DFWM and TC-RFWM (and optionally laser-induced fluorescence (LIF) and cavity ring-down (CRD) spectroscopy) is performed perpendicularly to the molecular beam and $\approx5\,mm$ downstream from the nozzle/discharge exit.

For DFWM and TC-RFWM, one or two separately pumped dye lasers (narrowscan, Radiant Dyes) are used, respectively. The specified bandwidth of the systems is $\approx0.04\,cm^{-1}$. The quantitative reduction of the four-wave mixing signals to population densities requires careful control of the applied laser intensities. Therefore, the pulse energies are arbitrarily adjustable with a variable attenuator (Newport, M-935-10) and range typically from $\approx1\,nJ$ to a few millijoules per pulse depending on the molecular transitions involved. For the sensitive application of the nonlinear methods, a very homogeneous intensity distribution over the entire laser beam diameter is required. Therefore, the laser beams have been spatially filtered by 50 or 100 μm pinholes and a series of apertures over a path of approximately 2 m. A combination of optical components establishes the forward BOXCARS configuration.[42,44] The three input beams with $\mathbf{k_1}$, $\mathbf{k_2}$, and $\mathbf{k_3}$ generate a signal beam wave vector $\mathbf{k_4}$ which is defined by the phase-matching condition, $\mathbf{k_1} + \mathbf{k_3} = \mathbf{k_2} + \mathbf{k_4}$. The parallel propagating incident laser beams pass through a quartz convex lens ($f = 1000\,mm$) and are focused through a window into the molecular beam interaction region. For the double-resonance experiment, one of the three incident beams ($\mathbf{k_2}$) is replaced by a laser beam of a different frequency (PROBE beam) to establish the forward BOXCARS configuration for TC-RFWM.[42,48,50,69] The equal-frequency input beams ($\mathbf{k_1}$ and $\mathbf{k_3}$) are commonly referred to as PUMP beams.

The four-wave mixing signal is recollimated by a second quartz lens ($f = 1000\,mm$). Then it is allowed to propagate $\approx3\,m$ through several irises as well as optical and spatial filters to remove interfering scattered light and unwanted fluorescence. Further reduction of stray light is achieved by a spatial filter consisting of a 30-mm focal length lens and a 50-μm pinhole in front of the photomultiplier tube (PMT). The substantial SNRs require a PMT of high dynamic range (Hamamatsu H3177). Furthermore, signal intensities observed occasionally in this experiment require attenuation by neutral density filters up to ND5 in front of the PMT. A digital oscilloscope (LeCroy LC564A) and a PC were used to acquire and store data for further processing. A typical signal is averaged 20 times for each scan step (0.01–0.04 cm^{-1} increment). Absolute wavelength calibration of the dye laser is achieved by
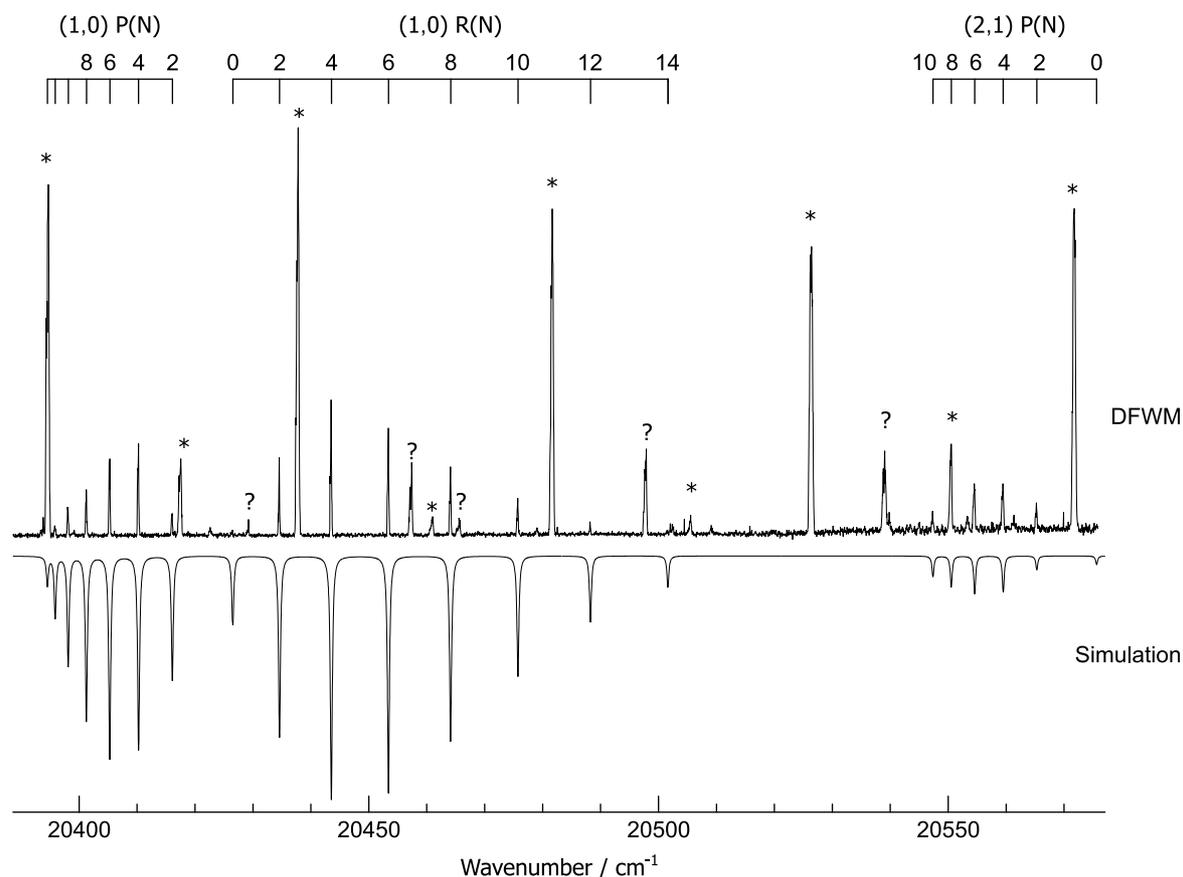
Figure 1. DFWM of two sequence bands ($\Delta v = 1$) in the $\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Sigma_g^+$ electronic system of C_2^-. The rotational assignments P(N) and R(N) indicate P and R branch transitions from the rotational level N of the ground state, respectively. Shown inverted is a simulation of the dimer anion by adapting molecular constants from the literature.[12] For the computation, a Boltzmann temperature distribution of $T_{rot} \approx 150$ K and $T_{vib} \approx 1500$ K are assumed. In addition, strong features due to high J levels of the neutral C_2 molecule are present in the spectra and marked by asterisks. The origin of transitions labeled with a question mark are unclear but probably due to perturbations or inaccurate molecular constants of high J levels in the Swan system of C_2. See text for details.

using a wavemeter (High Finesse/Ångstrom WS6) with a specified absolute accuracy of $\approx$600 MHz ($\approx$0.02 cm^{-1}).

Results

A DFWM spectrum around 20 500 cm^{-1} exhibiting the P and R branches of the (1,0) and (2,1) vibrational bands in the $\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Sigma_g^+$ electronic transition of C_2^- is shown in Fig. 1. As mentioned in the introduction, the carbon dimer anion is well characterized and its assignment is straightforward. The rotational transitions are indicated in figure. Only P and R branches are observed as expected for a $\Sigma - \Sigma$ transition. The nuclear spin statistics allows observations of even levels only. The simulation of the absorption spectrum is shown inverted by taking into account line positions and Hönl–London factors from the pgopher[70] program package and adopting the relevant rotational constants for the ground and excited state from the literature.[12] Several investigations in this laboratory[50] and by other groups[54,71–74] have shown that for carefully controlled conditions of the experiment (i.e. collision-free environment of the molecular beam, $I \cong I_{sat}$, parallel polarization of the input beams) the DFWM signal expression is given by the relation $I_{DFWM} \propto N''^2\mu^4$, where N'' and μ are the number density in the lower rotational state and transition dipole moment, respectively. Therefore, the com-

puted line positions and squared intensities are convoluted with a Lorentz line shape exhibiting a bandwidth of 0.4 cm^{-1}. The ground state population is obtained by assuming a Boltzmann distribution at a rotational temperature of $\approx$150 K. Because the strongest signals are obtained close to the slit-nozzle orifice at a distance of $\approx$5 mm, rotational cooling is not completed and explains the rather high temperature. Even less effective is the cooling of the vibrational degrees of freedom in a supersonic expansion ($T_{vib} \gg T_{rot}$). In fact, to obtain agreement with the measured spectrum, a vibrational temperature, T_{vib}, of $\approx$1500 K is assumed.

Apart from the lines assignable to the carbon dimer anion, pronounced transitions are observed in this spectral region that are attributed to the neutral carbon dimer. The intense transitions are due to the unresolved spin triplets of high J-levels ($J \gtrsim 80$) of the (0,0) band of the Swan $d^3\Pi_g - a^3\Pi_u$ transition. These transitions are labeled with asterisks in Fig. 1. Assignments are performed by utilizing the pgopher program[70] and using molecular constants from Tanabashi et al.[75,76] The origin of this high-temperature component of C_2 in the molecular beam is not clear, but it has been observed in other studies[77] utilizing the discharge source with the C_2H_2 precursor. In addition, a few transitions are marked with question marks that are not modeled accurately. Note, that the centrifugal distortion constants are not sufficiently determined
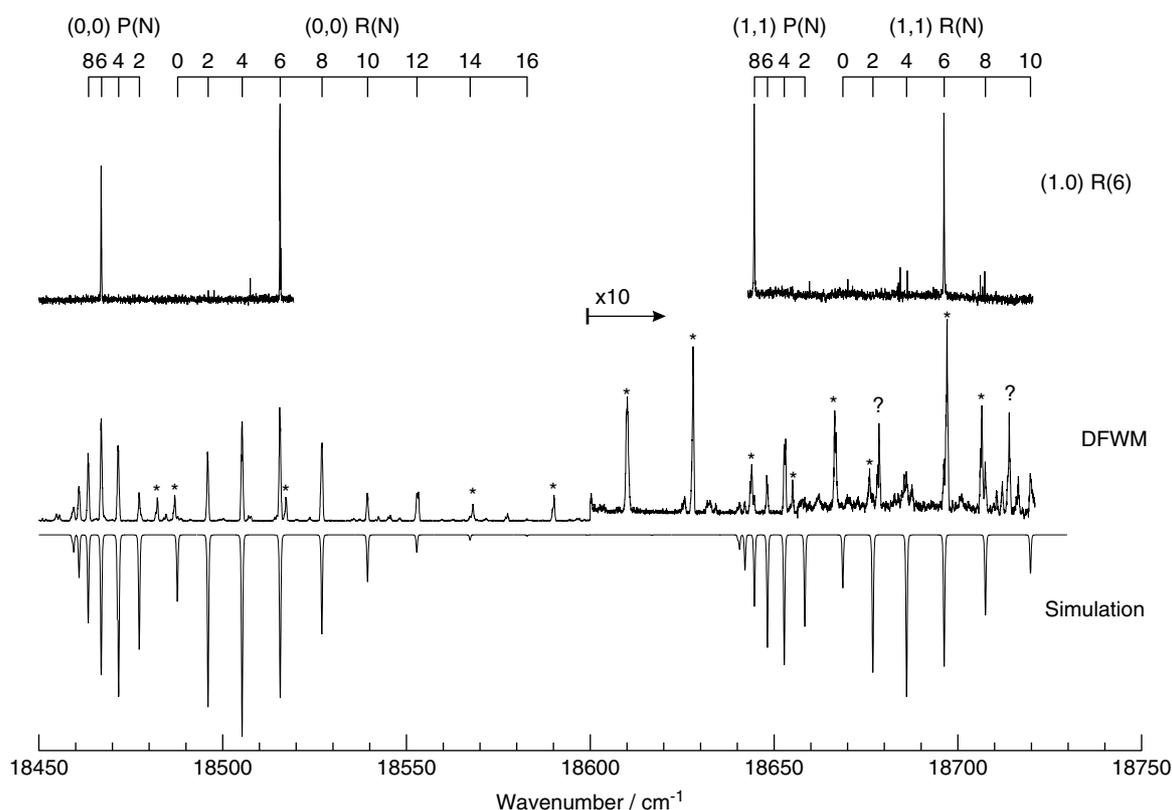
Figure 2. DFWM and TC-RFWM of C_2^- in the (0,0) and (1,1) sequence bands of the $\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Sigma_g^+$ electronic transition. An overall good agreement is observed by comparing the DFWM spectrum with the simulation. Numerous additional transitions are present that are mostly assignable to the neutral carbon dimer (*). The origin of transitions labeled with a question mark is unclear, but is probably due to perturbations or inaccurate molecular constants of high J levels in the Swan system of C_2. The TC-RFWM scans at the top trace unambiguously reveal the (1,1) P(8) and (1,1) R(6) transitions of the anion that are obscured in the one-color DFWM spectrum by Swan band transitions of the neutral C_2. See text for details.

for these high J levels. Furthermore, several rotational transitions in the Swan band of C_2 are disturbed by close-lying electronic states ($b^3\Sigma_g^-$, $X^1\Sigma_g^+$ and $B^1\Delta_g$) and their positions cannot be predicted by the simulation. Unfortunately, a global rotational analysis including perturbations has not yet been performed. A deperturbation study of the $d^3\Pi_g$ Swan state by applying double-resonant four-wave mixing methods is underway in our laboratories.[77]

In spite of these additional transitions appearing in the spectrum, the spectrum of the carbon dimer anion is clearly discernible. Owing to the supersonic cooling, the P and R branches display only J levels up to ≈ 14 and no band head is visible. The observation demonstrates that the four-wave mixing experiment established in our laboratory is applicable to the sensitive detection of vibrationally excited negative ions. The detection limit for the carbon dimer anion, C_2^-, investigated in this work compares well with the sensitivity obtained by cavity ring-down spectroscopy in a similar molecular beam/discharge environment and is approximately 10^7 anions/cm^3.[17] The excellent sensitivity of the method suggests that DFWM might serve as a general tool for the study of rotationally resolved vibronic transitions of ions.

In addition, similar sensitivities are measured for the double-resonant variant of the method. Figure 2 shows, in addition to the DFWM spectrum in the $\Delta\nu = 0$ sequence band region around 18 600 cm^{-1}, two traces that have been obtained by tuning the PUMP laser to the R(6) rotational transition in the (1,0) band at

20 453.4 cm^{-1}. A subsequent PROBE scan in the vicinity of the (0,0) band (top trace, left) displays two transitions only, which share the lower level labeled by the PUMP laser ($N'' = 6$ and $v'' = 0$ of $\tilde{X}^2\Sigma_g^+$): (0,0) P(6) and (0,0) R(6). A scan in the (1,1) band region (top trace, right) reveals P(8) and R(6), both sharing a common upper state with the PUMP laser ($N' = 7$, $v' = 1$ of $\tilde{B}^2\Sigma_u^+$). As for the $\Delta\nu = 1$ region, numerous transitions are present in the DFWM measurement of the $\Delta\nu = 0$ band due to the strong Swan band system of the neutral carbon dimer. In particular, the (1,1)P(8) and (1,1)R(6) transitions that are unambiguously observed by TC-RFWM at 18 643.8 and 18 697.0 cm^{-1} are obscured by C_2 lines in the DFWM spectrum. For example, the (1,1)R(6) line appears as a minor shoulder of the more intense C_2 line. The simplification of the complex one-color spectrum due to the restrictive double-resonance selection rules demonstrates the substantial selectivity of TC-RFWM in a situation where multiple components generate a congested one-color spectrum. The experiment in the (1,1) band region suggests that rotational characterization of high-lying vibrational states on the ground potential energy surface of anions is feasible by the stimulated emission pumping (SEP) capabilities of TC-RFWM.[48,63]

Summary and Conclusion

In this work, DFWM and TC-RFWM is applied, for the first time to the best of our knowledge, for the detection of an anion. It is demonstrated that the methods are sufficiently sensitive to detect

C_2^- in a molecular beam environment that has been generated by discharging a C_2H_2/argon mixture prior to supersonic expansion. A detection limit of 10^7 particles/cm^3 is inferred from a comparison with CRD experiments. Such a sensitivity is among the highest achieved by applying four-wave mixing methods. In addition, it is shown that the two-color variant exhibits a similar sensitivity. We conclude that optical double-resonance experiments of other anions (or radicals at low concentrations) might be feasible. Often, electronic states of anions are above the detachment threshold of the electron. Since the four-wave mixing methods are based on absorption, these states remain accessible for spectroscopic investigations and are, therefore, complementary to LIF or auto-detachment[78] techniques.

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