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

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Two-color resonant four-wave mixing spectroscopy can be used for the sensitive and selective characterization of negative ions in a molecular beam environment. Results are shown for C_2^- produced by an electric discharge in a mixture of acetylene and Argon. The plasma expands immediately after the discharge into vacuum forming a supersonic beam containing C_2-anions. High signal-to-noise ratios show that the preparation technique is suited for the application of high-resolution optical double-resonance spectroscopy.

Introduction

Negatively charged molecular ions are of relevance in astronomy, in the upper atmosphere, in electrical discharges, and in combustion. Anions are present in most combustion system and are assumed to play an important role in reactions forming pollutants like soot and aerosols from aircraft-engines[1-4]. In a recent work, Warnatz and coworkers[5] included negative ions in the chemical reaction mechanism for the modeling of a fuel-lean methane-oxygen flame. Detailed reaction mechanisms involving negatively charged species are required for assessing the kinetics prevalent in the processes of technical applications. In spite of their importance only few anion species are spectroscopically characterized, - reflecting the notorious difficulty to prepare anions in sufficient abundance. Often, anions are generated in a plasma where numerous, more abundant, neutral- and cation-species coexist whose spectra may overlap. Therefore, a high selectivity is required to disentangle the spectral features of anions among all other light emissions. An additional challenge for spectroscopic investigations of anions is the typical absence of stable electronically excited states that can not exist due to the low binding energy of the excess electron. Nevertheless, rotationally resolved electronic spectroscopy of valence or dipole bound states has been achieved for a number of anions. One of the prominently investigated anion is C_2^- [6-9].

We applied degenerate four-wave mixing (DFWM) and two-color resonant four-wave mixing (TC-RFWM), two background-free and highly sensitive methods, to C_2^-. DFWM and TC-RFWM are nonlinear spectroscopic tools exhibiting high signal-to-noise ratios due to 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 probing the signal beam at remote distances. The resulting high sensitivity renders the techniques applicable to species that are present in very low concentrations. This property has been successfully exploited for DFWM measurements of trace species in low pressure cells, flames and molecular beams[10-14]. The nonlinear methods are often complementary to the more conventional linear spectroscopic techniques. Because four-wave mixing is based on absorption, the signal intensity is insensitive to the lifetime of the upper level[15]. As a consequence, the large and important category of molecules, exhibiting non-fluorescing or pre-dissociative states, are accessible. Recently[16] it has been shown that the high temporal resolution of four-wave mixing spectroscopy on the order of a few ns is sufficient to discriminate between different species in a discharged molecular beam on the basis of their time shifted nascency. This is in stark contrast to to cavity ring-down spectroscopy[17], which allows the assessment of time scales only in the µs-domain. An additional benefit is obtained 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 selectivity by intermediate level labeling is beneficial to the simplification of spectral congestion. 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[18].

Thus, owing to the background-free characteristics of nonlinear four-wave mixing techniques, an inherently optimal signal-to-noise ratio is obtained. However, nonlinear methods suffer from their quadratic dependence on species density and involved cross-sections. Nevertheless, in recent works, we have shown that DFWM and TC-RFWM techniques are sufficiently sensitive to yield substantial signal-to-noise ratios for transient species in a molecular beam that are generated in a pulsed

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electric discharge prior to supersonic expansion. For example, a signal-to-noise ratio up to 50000 for the rotationally resolved $A^1\Pi_u - X^1\Sigma^+_g$ transition of C_3 has been obtained by applying a cylindrical discharge source on an acetylene/argon mixture [19]. 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. Experiments with the C_2 and HC_4S radicals resulted in high signal-to-noise ratios and a DFWM sensitivity among the highest achieved.

We took four-wave mixing spectroscopy one step further and demonstrate its excellent sensitivity by applying the method to an anion produced in a supersonic slit-discharge. The obtained detection limit of $10^7/cm^3$ for the carbon dimer anion C^-_2 at a ns-time domain resolution compares well with the sensitivity of the much slower cavity ring-down spectroscopy in a similar molecular beam environment.

A DFWM spectrum around 18600 cm^{-1} exhibiting the P and R branches of the (0,0) and (1,1) vibrational bands in the $B\ ^2\Sigma^+_u - X\ ^2\Sigma^-_g$ electronic transition of C^-_2 is shown in Fig. 1. The inverted trace represents a simulation of the absorption spectrum taking into account the line positions and Hönl-London factors from the pgopher[20] program package and adopting the relevant rotational constants for the ground and excited states[21]. Computed line positions and intensities are convoluted with a Lorentz line shape exhibiting a bandwidth of 0.4 cm^{-1}.

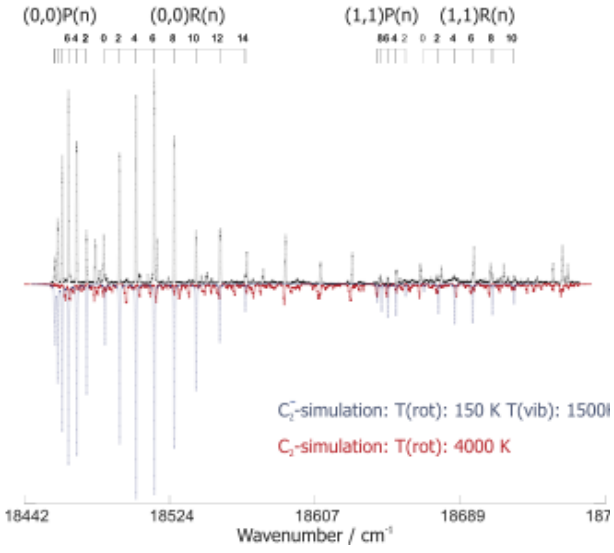

Fig. 1: A DFWM spectrum around 18600 cm^{-1} exhibiting the P and R branches of the (0,0) and (1,1) vibrational bands in the $B\ ^2\Sigma^+_u - X\ ^2\Sigma^-_g$ electronic transition of C^-_2.

References

1. Calcote, H.F., D.B. Olson, and D.G. Keil, Are ions important in soot formation? Energy \& Fuels, 1988. 2(4): p. 494--504.
2. Rodrigues, J.M., et al., Evolution of charged species in propane/air flames: mass-spectrometric analysis and modelling. Plasma Sources Science and Technology, 2007. 16(1): p. 161--172.
3. Starik, A.M., et al., Modeling of sulfur gases and chemiions in aircraft engines. Aerospace Science and Technology, 2002. 6(1): p. 63--81.
4. Stevens, R., et al., Measurement of nitric oxide concentration in a spark-ignition engine using degenerate four-wave mixing. Combustion and Flame, 2007. 148(4): p. 223--233.
5. Prager, J., U. Riedel, and J. Warnatz, Modeling ion chemistry and charged species diffusion in lean methane-oxygen flames. Proceedings of the Combustion Institute, 2007. 31(1): p. 1129--1137.
6. Lagerqvist, A. and G. Herzberg, A NEW SPECTRUM ASSOCIATED WITH DIATOMIC CARBON. Canadian Journal of Physics, 1968. 46(21): p. 2363.
7. Lineberger, W.C. and T.A. Patterson, Two photon photodetachment spectroscopy: The C-2 2[sigma] states. Chemical Physics Letters, 1972. 13(1): p. 40--44.
8. Shan-Shan, Y., et al., Study of hot bands in the B2 Σ +u-X2Σ +g system of C-2 anion. Chinese Physics, 2003. 12(7): p. 745--749.
9. Yokoyama, K., et al., Autodetachment spectroscopy and dynamics of vibrationally excited dipole-bound states of H2CCC-. The Journal of Chemical Physics, 1996. 105(24): p. 10706--10718.
10. Mazzotti, F.J., et al., Electronic spectra of radicals in a supersonic slit-jet discharge by degenerate and two-color four-wave mixing Physical Chemistry Chemical Physics, 2007. published online( ): p. DOI: 10.1039/b712737e.
11. Tulej, M., et al., Multiplex spectroscopy of stable and transient species in a molecular beam. Journal of Raman Spectroscopy, 2007. 38(8): p. 1022-1031.
12. Tulej, M., et al., Degenerate and two-color resonant four-wave mixing applied to the rotational characterization of high-lying vibrational states of formaldehyde ((A)over-tilde, (1)A(2)). Journal of Raman Spectroscopy, 2006. 37(1-3): p. 376-383.
13. Tulej, M., et al., Comparative study of degenerate four-wave mixing and cavity ringdown signal intensities of formaldehyde in a molecular beam. Journal of Raman Spectroscopy, 2006. 37(6): p. 680-688.
14. Tulej, M., et al., Photo-fragment excitation spectroscopy (PHOFEX) by DFWM and LIF: propensities for H2CO -> HCO+H near the S-o threshold. Journal of Raman Spectroscopy, 2005. 36(2): p. 109-115.
15. Farrow, R.L., D.J. Rakestraw, and T. Dreier, Investigation of the Dependence of Degenerate 4-Wave-Mixing Line-Intensities on Transition Dipole-Moment. Journal of the Optical Society of America B-Optical Physics, 1992. 9(10): p. 1770-1777.
16. R. Raghunandan, F.J.M., R. Chauhan, M. Tulej, J. P. Maier, submitted to Journal of Physical Chemstry A., 2009.

17. O'Keefe, A. and D.A.G. Deacon, Cavity Ring-Down Optical Spectrometer for Absorption-Measurements Using Pulsed Laser Sources. Review of Scientific Instruments, 1988. 59(12): p. 2544-2551.
18. Radi, P.P., et al., Stimulated emission pumping by two-color resonant four-wave mixing: rotational characterization of vibrationally excited HCO ((X)over-tilde(2)A '). Journal of Raman Spectroscopy, 2003. 34(12): p. 1037-1044.
19. Tulej, M., et al., Multiplex spectroscopy of stable and transient species in a molecular beam. Journal of Raman Spectroscopy, 2007. 38(8): p. 1022--1031.
20. Western, C.M., PGOPHER, a program for simulating rotational structure. 2007.
21. Jones, P.L., et al., Photodetachment Spectroscopy of C-2(-) Autodetaching Resonances. Journal of Chemical Physics, 1980. 73(9): p. 4419-4432.