Electronic spectra of radicals in a supersonic slit-jet discharge by degenerate and two-color four-wave mixing

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Four-wave mixing techniques have been used for the measurement of electronic transitions of cold transient species generated in a supersonic slit-jet discharge expansion. The origin band of the d'Πg→a'Πu system of C2 and A'Π3/2→X'Π3/2 electronic transition of HC4S were recorded. A signal-to-noise ratio of 10^4 in the spectra was achieved, resulting in detection limits of 10^10 cm^{-3} for these two molecules. Application of selective two-color resonant four-wave mixing is used for the spectral assignment utilizing the double-resonance nature of the method. The combination of these techniques with a slit source proves to be a sensitive approach for the detection of transient molecules in a molecular beam discharge.

Introduction

Electronic spectra of unsaturated carbon-chain radicals and ions produced in a supersonic discharge have been extensively studied during the last two decades by laser techniques, with important implications for astrophysics.1 These sources offer the advantage of producing a full class of carbon-bearing radicals, starting with a simple precursor, namely acetylene. Furthermore, the internal temperature of the molecules produced in a discharge followed by a supersonic jet expansion into vacuum is low enough to enable precise analysis of their spectra because the ground-state population is limited to the lowest J levels. Owing to the low density of the species present in the plasma, sensitive optical techniques are required for such measurements. Linear techniques such as absorption-based cavity ringdown spectroscopy (CRDS),2 laser-induced fluorescence (LIF)3,4 and resonant-enhanced multi-photon ionization (REMPI)5 and its double-resonance variant6 were successfully applied to the study of several of these systems. Although it is relatively easy to implement, CRDS is based on long line-of-sight absorption and has no selectivity, especially when spectral features overlap. Furthermore, CRDS is inappropriate for detecting transitions which are broadened by the short lifetime of upper states.7 LIF is inherently background-free and has extensively been applied to plasmas in luminous and harsh environments; however, it is only suited for systems which exhibit reasonably large fluorescence quantum yields and cannot be used to study systems that have unstable (dissociative or predissociative) excited electronic states. REMPI is limited to neutral molecules but its mass-selectivity provides unambiguous assignment for different species. In the case of complex, overlapping spectral features, linear techniques fail to unambiguously assign rotational lines within the same spectral system.

The use of a technique which would not share these disadvantages would be a valuable spectroscopic tool to study transients. Degenerate four-wave mixing (DFWM) and its variant two-color resonant implementation (TC-RFWM) appear to be good candidates for this task. The technique offers many advantages. First of all, it is background-free and produces a coherent signal which can be discriminated from scattered radiation.8 It has also proven to be highly sensitive, with obtained signal-to-noise (S/N) ratios as high as 10^4 with the species concentrations usually present in a discharge.9 Furthermore, it benefits from a large dynamic range. It does not suffer from fluorescence quenching10,11 and offers the unsurpassed possibility to perform resonant spectroscopy which, given simple selection rules, leads to spectra that are unambiguously assigned, even in the case of overlapping lines within the same system. This has lead to the understanding of molecular structure and dynamics in the case of high vibrational excitation.12,13 The TC-RFWM spectrum of highly excited states of NH3 was recorded in a room temperature gas cell14 with ten-fold improved sensitivity compared to previous measurements made with DFWM and rotational constants of ground-state vibrational levels of HCO were accurately determined,15 proving that TC-RFWM provided an increase in spectral sensitivity and selectivity compared to the degenerate case. It is, however, a technique difficult to implement which suffers practically from complex saturation effects such as line broadening with laser power. In fact, because the intensity at which a line saturates is inversely proportional to the strength of the observed transitions, the net result can vary for different spectral regions and lines if care is not taken in controlling the laser power. Moreover, it sometimes requires a powerful laser source capable of delivering millijoules per pulse and it is very sensitive to beam alignment as well as beam profile.
In a pioneer experiment, the potential of DFWM for monitoring the OH radical in combustion environments was reported.\textsuperscript{16} Following this work, four-wave mixing (FWM) measurements have been carried out in the gas phase as a diagnostic in combustion\textsuperscript{8,17–19} and in reacting plasmas.\textsuperscript{20,21} However, up until now, the FWM technique was used for measurements in molecular free-jet expansions only for a limited class of relatively small molecules and radicals, namely formaldehyde,\textsuperscript{22,23} SO\textsubscript{2},\textsuperscript{24,25} SiC\textsubscript{2},\textsuperscript{26} C\textsubscript{2}H\textsubscript{2},\textsuperscript{27} CS\textsubscript{2},\textsuperscript{28} C\textsubscript{3}\textsuperscript{1,2,29} generated by laser vaporization, predissociation spectroscopy of NO\textsubscript{2}\textsuperscript{30,31} and, more recently, C\textsubscript{2} by degenerate and two-color variant in a supersonic discharge.\textsuperscript{9}

In the present work, we report the detection of C\textsubscript{2} and of HC\textsubscript{4}S in a supersonic slit-jet discharge with degenerate and two-color resonant FWM. The two-color scheme provides unambiguous assignment of the rotational spectra for HC\textsubscript{4}S. To date, measurements done with the FWM technique on C\textsubscript{2} have been carried out only in high-temperature (3000 K) oxy-acetylene flames.\textsuperscript{32–34} Sulfur-terminated carbon chains are of interest in astronomy due to the relatively large cosmic abundance of this non-metallic element.\textsuperscript{3} Recently, the electronic spectrum of the Α 2Π\textsubscript{3/2}−Χ 2Π\textsubscript{1/2} system of HC\textsubscript{4}S produced in a supersonic discharge has been studied by LIF\textsuperscript{4} and dispersed fluorescence.\textsuperscript{5} In the latter, the authors report detection of several vibrational states in the electronic ground state, while in the former a rotationally resolved spectrum is achieved with a 0.02 cm\textsuperscript{−1} laser linewidth and spectroscopic constants are derived for several of these vibronic transitions.

**Description of four-wave mixing**

The theory of DFWM involves the third-order susceptibility tensor.\textsuperscript{35} In spite of the fact that the higher-order polarizations responsible for nonlinear optical phenomena are small, the signal intensities in the four-wave mixing process can be large due to its strong dependence on laser power, concentration and interaction length. Moreover, if one or more of the interacting frequencies are close to one- or multiphoton transitions, nonlinear susceptibilities can be greatly enhanced. FWM may be thought of as a resonant variant of coherent anti-Stokes Raman spectroscopy (CARS).\textsuperscript{21} A qualitative explanation of the phenomenon is that two beams (referred to as pump beams) interfere in the medium inducing macroscopic variations in the ground- and excited-state density and/or polarization, forming a Bragg grating. When the third beam (probe) is resonant with a second transition (it is the same in the degenerate case) having in common upper- in stimulated-emission pumping (SEP) spectroscopy or lower-state (UP transition), it gets reflected off the grating and its direction is given by the Bragg phase-matching condition.\textsuperscript{36} Fig. 1 shows energy-level diagrams for the three aforementioned spectroscopic techniques. The technique works well even with short-lived upper states since the grating formed by the lower-state density modulations and causing probe-beam reflection remains long-lived. The coherent laser-like signal beam allows a high collection efficiency and stray light is efficiently suppressed by remote probing. Under the unsaturated regime, the TC-RFWM intensity is given by:

\[
I \propto N^2 I_1^2 I_2 I_3 \times G(\varepsilon_1 \varepsilon_2 \varepsilon_3 J)^2
\]  \hspace{1cm} (1)

where \(I_1\), \(I_2\) and \(I_3\) are the intensities of the three incident beams, \(N\) is the population of the lower level, \(B_1\) and \(B_3\) are terms proportional to the dipole moments of the pump and probe transitions respectively, and depend also on the rotational number \(J\) of the transitions, \(G\), a term which accounts for the geometry of the interaction of the molecule with the electric fields in the laboratory frame, depends on the polarization vectors of the four beams (\(\varepsilon\)) and on \(J\). The reader should note that expression (1) depends quadratically on the population of the lower state of the pump transition, just as its degenerate counterpart does.

Formula 1 was used for making two-color spectral simulations: pump transitions were weighted by a Gaussian lineshape centered at the pump wavelength (FWHM was chosen as measured in the experimental spectrum). The corresponding SEP and UP transitions were then weighted by the factor \(N_1 B_1 B_3\), convoluted with a Gaussian and added in the spectrum which was squared so that intensity of isolated lines is in accordance with Formula 1. \(N_1\) is computed by assuming a Boltzmann distribution of the rotational states and the \(G\) factor, which levels off for \(J > 3\), was not taken into account.

A forward "box" (as beams are directed through the diagonals of a rectangular parallelepiped) cross-beams CARS geometry (known as BOXCARS,\textsuperscript{38} see Fig. 2) configuration was chosen, for which virtually all generated photons can be detected, in contrast to the Doppler-free phase-conjugate arrangement,\textsuperscript{39} for example, resulting in an increased sensitivitiy. The polarization of the four interacting beams was vertical in the laboratory frame.

**Experimental**

**Ion source**

Radicals were generated by pulsing a 0.7–1% acetylene (with 0.3% CS\textsubscript{2} for HC\textsubscript{4}S measurements) mixture in argon through the 30 × 0.3 mm (or 30 × 1.0 mm) slit-jet nozzle. A voltage of \(-600\) to \(-1000\) V was applied to the electrodes. The timing
pump beams (of the same frequency), I overlapped the beams in the center of the vacuum chamber, collinear components and a lens of 1000 mm focal length electric mirrors and beamsplitters divided the light into three in order to obtain a homogeneous profile. Broadband di-

was done with a wavemeter. The beam was spatially filtered

spectral range with a 0.10 cm^3 307 was used allowing continuous coverage of the 485–550 nm

operated at 20 Hz produced pulses of 8 ns duration. Coumarin

A dye laser pumped by the third harmonic of a Nd:YAG laser

Four-wave mixing setup

A dye laser pumped by the third harmonic of a Nd:YAG laser operated at 20 Hz produced pulses of 8 ns duration. Coumarin 307 was used allowing continuous coverage of the 485–550 nm spectral range with a 0.10 cm^{-1} linewidth. An intracavity etalon enabled reduction of the laser linewidth by a factor of 5. The laser energy was of the order of 1 mJ per pulse and variable neutral-density filters were used to reduce the laser-beam intensity because saturation of the FWM signal results in broadening of the absorption lines. Calibration was done with a wavemeter. The beam was spatially filtered in order to obtain a homogeneous profile. Broadband dielectric mirrors and beamsplitters divided the light into three collinear components and a lens of 1000 mm focal length overlapped the beams in the center of the vacuum chamber, near the tip of the nozzle. The crossing angle was 1.7° while the beam diameter was about 2 mm before the focusing lens, defining an overlapping region with the plasma produced by the slit source of 30 mm in length. The collection optics consisted of a series of spatial filters set on a 4-meter path which efficiently rejected the unwanted stray and scattered light. Alignment was performed by positioning a thin quartz cell containing a dye (absorber) in the interaction region. The output from the detector was sent to a fast 400 MHz digital oscilloscope. The area of the PMT signal was calculated and recorded. Typically, spectra were obtained by averaging the FWM signal on 20–40 laser shots. For the two-color experiment, a dye laser with a 0.15 cm^{-1} linewidth pumped by a separate Nd:YAG laser was used as the probe. Timing between lasers was electronically controlled by a pulse generator. A schematic diagram of the TC-RFWM setup is shown in Fig. 3.

Cavity ringdown spectroscopy setup

A standard CRDS setup for pulsed radiation was used. The cavity was formed by two highly reflective plano-concave mirrors with 1-meter radii of curvature (99.98% reflectivity at 500 nm) separated by a distance of 52 cm. The input laser beam was matched to the TEM_{00} mode. The radiation leaking out from the rear mirror was collected by a photodiode with amplifier, in front of which a broadband filter rejected the emission from the discharge. The ringdown curves were fitted by a home-made high-speed program. As CRDS is not a zero-background technique, the discharge was intermittently turned off every other laser pulse so that correction of the background was possible. Typical ringdown times measured were about 18–20 μs with an empty cavity and about 15 μs when the discharge was turned on with no absorption at the laser wavelength.
Results and discussion

Detection of C2 by degenerate four-wave mixing

The recordings of the $^3\Pi_g-a\ ^3\Pi_u$ electronic system of C2 by DFWM in high-temperature flames have been reported, and make the molecule well suited for initial experiments. A spectrum of the C2 Swan-system origin band is shown in Fig. 4a. The numerous transitions between the triplet states produce a high density of lines, with a clear progression of triplets in the high $J_s$ of the R branch due to the spin multiplicity. The spectral contour fitting made with PGOPHER software by using spectroscopic constants available in the literature leads to an estimate of the rotational temperature of about 140 K. The DFWM signal detected was intense, resulting in a $S/N$ of the order of $10^4$ for the strongest transitions.

Experimental linewidth of the lines is nearly twice the linewidth of the probe laser, indicating that the experiments were done in the saturated regime. Under these conditions, the reproducibility in intensity of the spectral lines was improved as well as $S/N$ since the DFWM signal is not as highly dependent on shot-to-shot laser variations as in the unsaturated regime. Also shown are spectra obtained when the transition located at 515.020 nm is excited, which corresponds to the weak line $^3\Pi_{g}(6)$. With higher laser power, weak components originating from nearby lying transitions, i.e. the 60-fold-stronger $^3\Pi_{g}(6)$ transition and 7-fold-weaker $^3\Pi_{u}(2)$ are visible in the spectrum. This is interpreted as the laser-pump wavelength (FWHM of 0.004 nm) lying in the wings of the cubed FWM Lorentzian lineshape of the $^3\Pi_{g}(6)$ strong line, which is shifted 0.007 nm to the blue end of the spectrum (and of the $^3\Pi_{u}(2)$ line, shifted 0.001 nm to the red). When laser power is appropriately reduced, it is possible to excite only one transition (Fig. 5, trace c) and the two-color spectrum is unambiguously assigned to $^3\Pi_{g}(6)$. This illustrates the importance of laser-power control when performing spectroscopy with DFWM. It should be emphasized that the main advantage of the two-color RFWM compared to standard absorption techniques in analyzing complex molecular spectra: it provides excellent spectral selectivity and offers enough sensitivity for the detection of transient species produced in a supersonic discharge.

Detection of C2 by two-color four-wave mixing

The wavelength of the pump laser was tuned to a transition of C2 while the probe laser was scanned, resulting in spectra (Fig. 5) which can be unambiguously analyzed. When tuned to the $^3\Pi_{g}(3)$ transition: 2 SEP and 2 UP corresponding transitions were observed, one of each in the P and Q branches. The
Detection of HC₄S with DFWM

To date, FWM was not applied to middle-size or long carbon chains in a discharge. A strong FWM signal was observed when the laser was tuned to the origin band of the \( \tilde{A} \ \tilde{\Pi}_{3/2} \rightarrow \tilde{X} \ \tilde{\Pi}_{3/2} \) electronic transition of HC₄S. If the laser power was too high (several hundreds of mJ), saturation ensued. The spectrum would then display a broad envelope, showing no rotational structure. When the laser-power intensity was reduced (to 20–100 mJ), the P branch could be resolved without an intracavity etalon, as can be seen in Fig. 6a. The spectra were recorded 12 mm from the nozzle slit, where the temperature of the radicals is lower. With an intracavity etalon, the scan obtained (Fig. 6b) shows good agreement for the intensity and line position with the simulation. For these preliminary measurements, the rms of the fit in the line positions is 0.008 cm⁻¹ (see text). The relative intensity of the experimental spectrum was best matched to the simulation by contour fitting.

Fig. 6 (a) The \( \tilde{A} \ \tilde{\Pi}_{3/2} \rightarrow \tilde{X} \ \tilde{\Pi}_{3/2} \) origin band of HC₄S and DC₄S recorded by degenerate four-wave mixing. The linewidth of the laser was 0.1 cm⁻¹, small enough to resolve the individual rotational lines in the P branch. In the HC₄S spectrum, a vibronic component is present (see text). (b) Degenerate four-wave mixing spectrum of HC₄S recorded with an intracavity etalon. The inverted trace is the square of the simulation with a rotational temperature of 30 K and a Gaussian linewidth of 0.038 cm⁻¹, slightly larger than the estimated laser linewidth of 0.020 cm⁻¹. The rms of the fit in the line positions is 0.008 cm⁻¹ (see text). The relative intensity of the experimental spectrum was best matched to the simulation by contour fitting.

Detection of HC₄S with DFWM

When the pump laser was set to the spectrally unresolved band head, many corresponding transitions could be observed in the P branch as shown in Fig. 7, where a simulated two-color spectrum is also plotted. The intensity pattern of the isolated lines in the P branch is well reproduced by the simulation. However, the band head which consists of many overlapping lines and for which the total enhancement of the intensity depends on FWM process is broader than the simulation and a special treatment would be more appropriate. This spectrum illustrates the ability of TC-RFWM to disentangle overlapping spectral features in a congested band head. For this, it is sufficient to tune the pump laser on any of the observed P transitions and only two corresponding R transitions will be present in the TC spectrum if the correct saturation conditions are met.

Sensitivity of four-wave mixing

CRDS measurements were used to obtain the value of the concentrations of C₂ and HC₄S in the discharge. Owing to its capability of recording absolute absorption, CRDS is a self-calibrated technique. By using the oscillator strength previously measured \( (f = 0.029) \), a concentration of \( 10^{12} \) molecules per cm³ for C₂ (\( \tilde{a} \ \tilde{\Pi}_u \) state) in the plasma is estimated at a temperature of 140 K. With \( S/N \) of about 10⁶ for DFWM, the technique has a detection limit of \( 10^{10} \) molecules per cm³. This gives a sensitivity below \( 10^9 \) molecules per cm³ per rotational state, which is about distortion and spin–orbit coupling are obtainable by combining CRDS and four-wave mixing techniques.

Detection of HC₄S by two-color four-wave mixing

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the lowest detection limit achieved with this technique reported in the literature. In the case of HCS, using values of transition moments obtained by ab initio computations, a density of about $10^{14}$ molecules per cm$^3$ is inferred. The S/N ratio of $10^{9}$ yields a detection limit below $10^{10}$ molecules per cm$^3$. These results confirm the potential of the FWM technique for measuring unsaturated carbon chains in a planar-expansion discharge.

**Conclusion**

This paper presents electronic spectra of C$_2$ and HCS produced in a slit-jet discharge by the four-wave mixing technique. DFWM and TC-RFWM were used in the forward BOXCARS geometry. The technique produces a coherent beam which can be discriminated from laser scattering and plasma emission, resulting in high S/N spectra and a DFWM sensitivity among the highest achieved. It is illustrated that the two-color approach, applied to the $^3\Pi_u - ^3\Pi_g$ system of C$_2$ and the $^3\Pi_u - ^3\Pi_g$ electronic transition of HCS, provides a spectroscopic tool for unambiguous assignment while offering the possibility of disentangling overlapping components. The potential of using four-wave mixing in slit-jet discharges for studying radicals at low temperature is asserted.

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**References**