Selective Detection of Radicals and Ions in a Slit-Jet Discharge by Degenerate and Two-Color Four-Wave Mixing[†]

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Degenerate four-wave mixing (DFWM) was used to record the spectra of charged and neutral carbon-containing radicals generated in a pulsed discharge source within a supersonic slit-jet expansion. Detection limits of $\sim 10^9$ molecules cm^{-3} are achieved. The DFWM method allows a selective molecular detection by varying the discharge timings. Increased spectral selectivity is obtained by applying the two-color, doubly resonant four-wave mixing variant. This shows the potential of the techniques for sensitive and selective spectral analysis of radicals in discharges. The methods are successfully used for the detection of C_4H, HC_2S, and HC_4H^+ with signal-to-noise in the range of 10^2-10^4.

1. Introduction

Charged and neutral carbon radicals are of importance in various reactive environments, including planet atmospheres, combustion, and interstellar media. The means of their identification in situ as well as the information on the physical and chemical conditions present in the reactive medium has resulted in considerable interest in the laboratory detection of such species by spectroscopic techniques. This motivated such studies on several carbon-bearing radicals.[1,2] The laboratory and astronomical investigations in the millimeter-wave region lead to the identification of many carbon chains in space, including ions and radicals.[3] Measurements on these molecules are difficult because they are short-lived species generated in small number densities. Discharge and laser vaporization sources coupled to a supersonic jet expansion are, so far, the most effective techniques used to generate sufficiently large densities suitable for spectroscopic studies of these transients. Sources equipped with a circular expansion nozzle were coupled to methods such as photoelectron[4] and photodetachment[5,6] or resonance-enhanced multiphoton ionization (REMPI)[7] for the characterization of complex carbon molecules. These techniques have the advantage of offering mass selection but frequently are limited or difficult because of high ionization potentials in REMPI or inconvenient wavelength range. The pinhole source was also coupled to microwave,[8,9] laser-induced fluorescence (LIF),[10] cavity ring-down (CRDS),[11] and four-wave mixing (FWM) spectroscopies.[11,12] However, a high spectral congestion due to the various species present in the expansion may hinder the sensitivity and selectivity of the latter methods, resulting in overlapping spectra and sometimes higher background. This complicates the identification of their transitions.

Improvements to the detection sensitivity of CRDS have been made by a combination with the slit-jet expansion nozzle.[13] Several charged and neutral radicals were investigated and compared with astronomical observations.[14] In addition, the CRDS technique has been used as a plasma diagnostic method for gathering information on electron densities and temperature in electrical discharges.[15] The two main advantages offered by slit-jet sources in comparison with the circular pinhole jets combined with CRDS[16] are a significantly longer path length and, because of a unidirectional jet flow, nearly Doppler-free measurements. They are also convenient in spectroscopic applications because the species density decreases linearly with the distance from the slit instead of quadratically, as occurs with pinhole jets. Further increase in detection sensitivity is achieved by the adiabatic expansion that causes a drop in the internal temperature of the molecules so that only the lowest rotational levels are populated. Some of these features have been illustrated in studies of the hyperfine-resolved structure of the methyl radical in a nearly Doppler-free jet[17] and infrared high-resolution measurements on HD_2O^+.[18]

The slit-jet expansion discharge has also been recently coupled to resonantly enhanced four-wave mixing spectroscopy for the detection of HC_4S.[19] Initial studies showed that the sensitivity of DFWM can be significantly increased by several hundred compared with the use of a circular pulsed discharge source, which is in agreement with an earlier report and is in accordance with the quadratic dependence exhibited by DFWM with the interaction path length.[43] Estimations made on OH in a flame gave detection limits (DLs) of $\sim 10^{11}$ molecules cm^{-3} per quantum state for DFWM.[20] After these first investigations, the technique remained yet to be coupled to a supersonic expansion discharge. The precision required in the alignment procedure, involving the spatial positioning of three beams for which a high-quality transverse profile plays a crucial role in the sensitivity and the artificial background created by scattering sources (i.e., windows), makes this method relatively difficult to implement in comparison with pulsed CRDS or LIF.

In this article, we demonstrate that the combination of a slit-jet discharge source with the resonantly enhanced four-wave mixing method is a powerful tool in the spectroscopic detection of neutrals and ions generated in diluted plasmas, offering in addition the selectivity of the molecules studied. Further improvements in species selectivity and sensitivity are achieved by the application of a double-resonance variant of four-wave mixing (FWM), namely, two-color resonant four-wave mixing spectroscopy (TC-RFWM).[21] In this work, the potential of

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DFWM for the study of neutral and charged radicals generated in electrical discharges is evidenced by the detection of C_4H, HC_2S, and HC_4H^+. The first spectroscopic detection of ions produced in an electrical discharge by four-wave mixing spectroscopy is presented. In parallel with the DFWM measurements, the self-calibrated CRDS method was used to estimate the concentration of the ions and neutrals in the plasma.

2. Techniques

2a. Cavity Ringdown Spectroscopy. Cavity ringdown spectroscopy is a linear absorption method based on the measurement of the decay time of a light pulse trapped in a stable optical cavity formed by two highly reflective mirrors.[22] The characteristic decay rate of the radiation (referred to as the ringdown time) depends on the reflectivity of the mirrors and is related to the absorption of the species located inside the cavity. The ringdown time is on the order of 20 μs in the visible, which is achievable with available commercial mirrors. It is not a background-free technique because the physical processes involved (like scattering from the plasma) will increase the cavity losses. As discussed below, the main limitation resides in the long probing time of the technique because the method is applicable only to processes that last for a duration on the order of the ringdown time.

2b. Degenerate Four-Wave Mixing and Two-Color Resonant Four-Wave Mixing. DFWM is a coherent nonlinear process involving the third-order susceptibility tensor.[23] This technique was successfully applied to spectroscopy because of the signal enhancement occurring at atomic and molecular resonant energies. Although the mathematical formulation of the four-wave mixing theory is complex, its basics can be explained by the transient laser-induced gratings analogy.[24] Two coherent beams (pumps) of the same frequency, overlapping in space and time, create a population grating in the medium when tuned to a molecular transition, causing macroscopic variations of the index of refraction. A third beam (probe) is then diffracted by the induced grating when it comes into resonance with the pump transition and creates a fourth beam (signal) that is detected. The geometrical arrangement of the incident beams requires that the phase-matching condition is satisfied. When the pump and probe beams have the same wavelength, the technique is called DFWM; otherwise, two-color four-wave mixing. The latter is a double-resonance method and can be used to disentangle overlapping or congested spectra.[25] Analytical expressions of the DFWM signal have been either determined for a simplified theory of the saturable absorber[26] or derived from the diagrammatic perturbation theory.[27] Both approaches predict that under saturation conditions, the signal intensity depends quadratically on the number densities and the absorption cross section of the species of interest, making this technique liable for analytical studies.[28] It was successfully used for spectroscopy in flames,[29,30] gas cells,[31] and molecular beams,[11] and, unlike LIF, can also be used to measure short-lived, highly predissociative excited states.[32]

3. Experimental Section

3a. Source. The pulsed discharge slit has already been described.[16] The slit used was 30 × 1 mm^2. The high voltage applied was in the range of -400 to -1200 V, whereas the backing pressure was around 10 bar depending on the species measured. The average pressure in the vacuum chamber was kept to 0.05 mbar. The pulse valve was opened for 300 μs, and the discharge was on for 0.3−3 μs with the FWM technique. The pulse delay between the high voltage pulse and the laser was in the range of 4−10 μs, depending on the distance of the interaction region with the slit nozzle as well as the carrier being detected. The timing sequence was controlled by a delay pulse generator with a precision of 0.25 ns. Gas mixtures used for the efficient production of the HC_2S and C_4H radicals were $CS_2/C_2H_2/Ar$ (0.5/1/98.5%) and C_2H_2/Ar (1/99%), respectively. For the production of the diacetylene cation, the precursor was C_2H_2 (or C_4H_2) diluted in argon.

3b. Four-Wave Mixing Setup. The FWM configuration opted for was a forward BOXCARS[33] scheme for which virtually all signal photons are collected. The laser beam is divided into three components of equal intensity (with 70/30 and 50/50 beamsplitters) that are reflected by broadband mirrors and are focused by a 1000 mm focal length lens into the vacuum chamber. A pump crossing angle of approximately 1.5° and a beam diameter of ~2 mm before the lens define an interaction region of ~30 mm, therefore making use of the whole expansion length. For the TC-RFWM experiments, the pump beams were chosen so that the interference fringes were directed along the jet to avoid washing out of the gratings by the gas flow and, consequently, a decreased signal beam.[34] Because the signal beam created by the FWM process is coherent in nature, it is efficiently rejected against stray or scattered radiation by the use of spatial filters, irises, and a long path length from the interaction region to the detector. This enables the recording of background-free spectra, a high signal-to-noise (S/N) offering both high sensitivity and precise line positioning. The S/N achieved was on the order of $\sim 10^3$ for the strongest spectral lines of C_4H and HC_4H^+ and $\sim 10^4$ for HC_2S. The tunable radiation was delivered by two dye lasers pumped by a Nd/YAG laser operated at 20 Hz, delivering photons in 7 ns with approximately 0.06 cm^{-1} line width. Laser energy was kept in the 100 μJ per pulse range by neutral density filters. The data were collected by a photomultiplier tube and digitized by a fast oscilloscope. The signal was averaged for 2 to 3 s, equivalent to 40−60 laser shots, for all spectra presented.

Before taking the DFWM spectrum, the signal was optimized by studying its dependence on laser power and line shape. At low laser power, the DFWM signal is cubically dependent on laser intensity of the beams. For sufficiently large laser powers, the widths of the rotational lines can be severely broadened and may lead to line width splitting (saturation dip). In accordance with the DFWM theory, the line width of the rotational lines is dependent on the laser power. Under appropriate saturation conditions, the DFWM signal intensity is proportional to the square of the absorption cross section and number densities. Early experimental studies have also confirmed these theoretical predictions.[35] This saturation intensity is, of course, dependent on the selected species.

4. Results

4a. Species Selectivity in the Temporal Domain. The probing time of the DFWM technique is equal to the laser pulse duration (presently 7 ns). This is at least three orders of magnitude shorter than the time required for the operation of CRDS. To study transient species generated in the plasma, an optimal use of CRDS requires a discharge pulse duration of several tens of microseconds. Current observations show that at such timings, a large number of spectral carriers can be detected simultaneously, which results in congested spectra. The probing duration of DFWM offers the possibility of using short but intense high-voltage pulses while maintaining appropriate generation conditions. The application of a pulse in the sub-microsecond range, however, has a drastic effect on the temporal

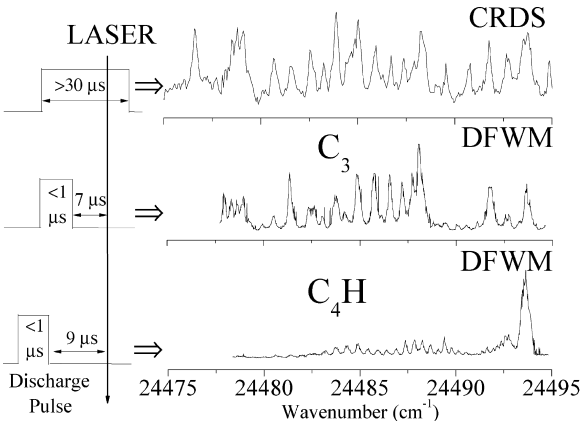

Figure 1. Selectivity offered by degenerate four-wave mixing combined with a short and intense discharge high-voltage pulse (submicrosecond range). Increasing the delay between the discharge and the laser by 2 μs enables disentanglement of the $\tilde{B}^2\Pi_i - \tilde{X}^2\Sigma^+$ (5_0^3) spectrum of C_4H, which overlaps a hot band of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ C_3 electronic transition. The top is a cavity ringdown scan that can be combined only with a discharge period of at least 20 μs, for which the C_3 and C_4H transitions overlap.

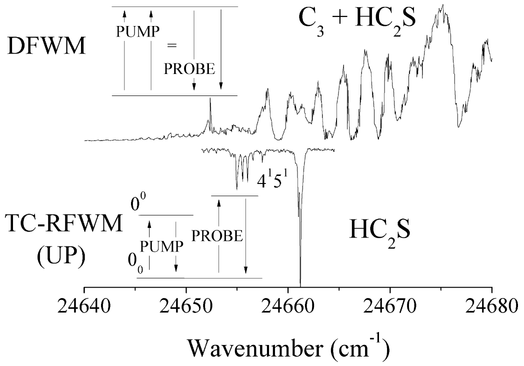

Figure 2. Scan showing the power of two-color four-wave mixing for disentangling overlapping spectra. Upper trace is a DFWM spectrum recorded near the origin band of the C_3 cometary system. A $CS_2/C_2H_2/$Ar (0.5/1/98.5%) precursor mixture was used. The $4_0^1 5_0^1$ band of the $\tilde{A}^2\Pi_{3/2} - \tilde{X}^2\Pi_{3/2}$ transition of HC_2S is blended with the C_3 $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ origin band transition (which is saturated). In the TC-RFWM case, where the pump wavelength is set to the origin band of HC_2S, scanning the probe frequency reveals the rovibronic spectrum of this selected species (inverted trace). The origin band of C_3 is no longer resonant and is absent.

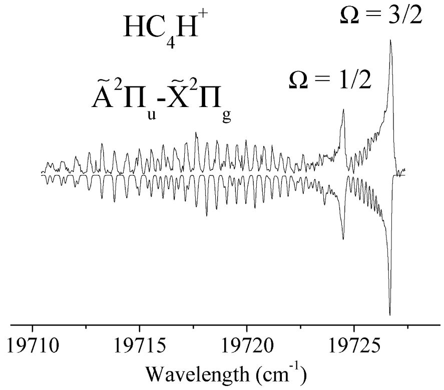

Figure 3. Square root of the degenerate four-wave mixing spectrum of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ electronic transition of the diacetylene cation (top trace) along with the simulation (reverted trace). The rotational temperature was determined to be 65 K, and the line width of single rotational transitions was about 0.1 cm^{-1}. The two spin−orbit components of HC_4H^+ overlap. The delay between the high voltage and the laser was set to 4 to 5 μs.

distribution of the radicals in the molecular beam. Although modeling of this process was not carried out, one can assume that the discharge pulse generates upstream, relative to the slit, a reservoir of radicals with approximately the same kinetic energies. The design of the pulsed discharge nozzle is such that the residence time of the molecules in this active region is on the order of a few microseconds.[15] These subsequently expand toward the lower pressure regions with speeds in accordance with their masses. The current experimental conditions generate a highly dense and short (1 μs) molecular pulse. It was observed that molecules with different masses travel through the interaction region at varying times (within the range of several microseconds). For neutrals, the lighter ones are measured at shorter laser-discharge delays. It is hence possible to discriminate the carriers by using short discharge pulses and appropriate time delays between the high voltage and laser firing. Under these conditions, efficient radical selectivity is achieved, which, in combination with a background-free signal, results in a highly sensitive spectroscopic detection. When carrying out experiments with CRDS, its limitations impose the use of a 20 μs long high-voltage pulse, generating a sufficiently long temporal distribution of the species for an efficient detection but with a price in selectivity. The experimental illustration of this is shown in Figure 1. The spectra recorded with DFWM are readily assigned to either a hot band of the C_3 $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ or to the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ or to the $\tilde{B}^2\Pi_i - \tilde{X}^2\Sigma^+$ electronic transition (5_0^3) of C_4H,[36] depending on the discharge delays, whereas the CRDS trace is rather congested. Notice that in the spectrum recorded with a longer laser-discharge delay (9 μs instead of 7 μs), the C_3 lines are completely absent.

4b. Species Selectivity by Two-Color Resonant Four-Wave Mixing. We obtained the TC-RFWM spectra by tuning the pump laser frequency to a molecular line while the probe laser was scanned. The recordings then show only the resonant transitions (i.e., involving a common state with the pump transition; either the upper state in stimulated emission pumping (SEP) or the lower state in the ground-state depletion UP[11] scheme) leading to simple and unambiguously assigned spectra, even in the case of congested features. By taking advantage of this, it is possible to disentangle a transition of HC_2S that overlaps with the origin band of the C_3 $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ system (Figure 2). The DFWM scan of the region shows the intense C_3 origin band in the same spectral region where a vibronic feature of the $\tilde{A}^2\Pi_{3/2} - \tilde{X}^2\Pi_{3/2}$ electronic transition of HC_2S is blended and for which a rotational analysis cannot be readily carried out. By tuning the pump to the R branch of the HC_2S origin and scanning the probe across the $4_0^1 5_0^1$ band, a rotationally resolved spectrum arising purely from HC_2S is obtained. These recordings exemplify the main advantages of using TC-RFWM for the study of transient molecules, namely, high sensitivity, species, and spectral selectivity.

4c. Detection of a Cation by Degenerate Four-Wave Mixing and Two-Color Resonant Four-Wave Mixing. The detection of C_2 and C_3 with S/N of $\sim 10^6$ and C_4H, HC_2S, HC_4S with S/N of $10^3 - 10^4$ suggests that other radicals, including ions, can be studied with this technique. The electronic transition of HC_4H^+ cation[37] was chosen to estimate the sensitivity of DFWM for charged molecules. Figure 3 shows the DFWM spectra recorded near the band origin of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ transition of HC_4H^+ by probing the ions close to the slit, near the region where the discharge is formed and where the density of the ions is the highest. This is the first detection of a polyatomic cation by DFWM in a supersonic expansion discharge. The two bandheads are due to the two spin−orbit components. The

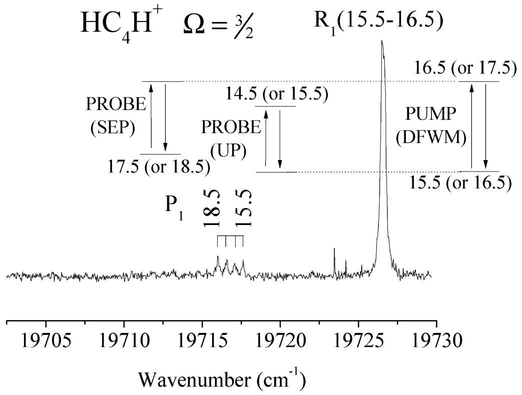

Figure 4. Two-color resonant four-wave mixing scan of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ electronic transition of HC_4H^+ obtained by setting the pump laser on the bandhead of the Ω = 3/2 spin−orbit component (at 19 726.60 cm^{-1}). Only two lines on the R_1 branch are excited, R_1(15.5) and R_1(16.5), resulting in four resonant lines in the P_1 branch. Because of the double-resonance character of the technique, the Ω = 1/2 component is absent from the trace, exemplifying the potential for disentangling overlapping features within the same spectroscopic system. The power of the two lasers was adjusted to enable the resolution of the individual rotational lines in the P_1 branch.

doublets are inverted so that the $^2\Pi_{3/2}$ component is the most populated, corresponding to the strongest R_1 branch. The rotational temperature according to the contour fit is around 65 K. Whereas in the case of the detection of neutrals, the delays between the laser and the discharge pulses are quite predictable and somewhat follow the kinetic rule (heavier species are slower than lighter ones), the detection of ions show some irregularities. For instance, to record the spectrum of HC_4H^+, a laser-discharge delay of 4 to 5 μs was applied, whereas one would expect a similar delay as in the detection of C_4H (9 μs), which has almost an identical mass. Although this behavior is not fully understood, it is partially due to the electrostatic effects caused by the DC high-voltage electrical field oriented downstream with the expansion and accelerating the positive ions.[15]

A rather unique application of TC-RFWM is the selective disentanglement of overlapping transitions belonging to the same carrier, as demonstrated in Figure 4. TC-RFWM enables a study of rotational features belonging to either spin−orbit component of the origin band of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ electronic system of HC_4H^+. The pump laser was set near the bandhead of the Ω = 3/2 component (at 19 726.60 cm^{-1}). The resonant transitions consist of the R_1(15.5) and R_1(16.5) (corresponding to the degenerate case) and of four lines in the P_1 branch, which are unambiguously assigned. The resonant lines in the Q_1 branch are too weak to be observed (by an order of magnitude). The lines in the P_1 branch are 10-fold weaker than those in the R_1 branch because of the relatively high rotational temperature of the species (∼65 K). However, because of the high S/N achieved, they are readily detected. This illustrates the ability of the technique to disentangle overlapping spectral features within the same spectroscopic system, as was previously demonstrated on nitrous oxide.[38]

4d. Sensitivity of Degenerate Four-Wave Mixing. Although hindered by a greater-than-linear dependence on number density, DFWM and TC-RFWM spectroscopies were proved to be sufficiently sensitive for the detection of less-abundant radicals generated in discharges. In fact, the quadratic dependence of the DFWM signal on the interaction length leads to a significant enhancement in sensitivity once combined with the slit-jet source and offers selective probing of the species when a short, intense discharge pulse is applied to the electrodes. The density of the neutrals determined from parallel measurements carried out by the self-calibrated CRDS yields a DL of around 10^9 molecules cm^{-3} for DFWM. Given the oscillator strength of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ transition of HC_4H^+ (∼0.04)[39] and an absorption coefficient measured by CRDS of ∼10^{-4} cm^{-1}, this yields a concentration of 3 × 10^{10} molecules cm^{-3} for the charged species. Because the S/N by DFWM is around 10^3, a DL of approximately 10^9 ions cm^{-3} was inferred. This is in accordance with earlier estimations made for selected radicals bearing similar intensities in the transition dipole moments (Table 1).

TABLE 1: Detection Limits (DL) Achieved by the Degenerate Four-Wave Mixing Technique for the Studied Radicals

	C_2[a]	HC_4S[a]	C_2^-[b]	HC_4H^+
S/N	10^6	10^3	$>10^2$	10^3
DL (mol·cm^{-3})	10^9	3×10^9	$<5 \times 10^8$	$\sim 10^9$
rotational temp (K)	140	30	250	65

[a] Ref 19. [b] $B^2\Sigma - X^2\Sigma_g^+$ (1−0) transition.[42]

5. Future Prospects

In addition to its high sensitivity, the technique offers a way to disentangle spectrally congested features via its double-resonance variant as well as the means to separate overlapping systems of radicals. Furthermore, using the SEP or UP schemes, it is possible to map out either rovibrational levels in the ground state or energetically high-lying electronic transitions, for which linear absorption techniques imply the use of not easily accessible frequency ranges. Other four-wave mixing schemes can be used in conjunction with the discharge source. For example, a backward BOXCARS scheme was carried out in a gas cell for the sub-Doppler spectroscopy of C_6H_6.[40] This arrangement can be combined with the supersonic slit-jet discharge and, in view of the DLs inferred in this work, seems to be a promising method when coupled to a high-resolution laser for the detection of linear chains with at least six carbon atoms, for which Doppler broadening limits the resolution of the rotational structure. The overall sensitivity can still be improved by changing the geometrical parameters of the experiment, such as slit length, beam crossing angles, and beam diameters. Spectroscopic detection of transient radicals broadens the perspective toward using DFWM and TC-RFWM for the investigation of their reactions. These two methods offer several possibilities for such studies, as was previously demonstrated with respect to molecules.[41] In view of the DLs obtained, the technique is promising for the detection and spectroscopic characterization of other neutral and charged species in the pulsed slit-jet supersonic expansion discharge.

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References and Notes

(1) Van Orden, A.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313.

(2) Jochnowitz, E. B.; Maier, J. P. *Mol. Phys.* **2008**, *106*, 2093.

(3) Thaddeus, P.; McCarthy, M. C. *Spectrochim. Acta, Part A* **2001**, *57*, 757.

(4) Xu, C.; Taylor, T. R.; Burton, G. R.; Neumark, D. M. *J. Chem. Phys.* **1998**, *108*, 1395.

(5) Osborn, D. L.; Leahy, D. J.; Cyr, D. R.; Neumark, D. M. *J. Chem. Phys.* **1996**, *104*, 5026.

(6) Tulej, M.; Kirkwood, D. A.; Maccaferri, G.; Dopfer, O.; Maier, J. P. *Chem. Phys.* **1998**, *228*, 293.

(7) Ding, H.; Schmidt, T. W.; Pino, T.; Boguslavskiy, A. E.; Güthe, F.; Maier, J. P. *J. Chem. Phys.* **2003**, *119*, 814.

(8) Endo, Y.; Kohguchi, H.; Ohshima, Y. *Faraday Discuss.* **1994**, *97*, 341.

(9) Sanz, M. E.; McCarthy, M. C.; Thaddeus, P. *J. Chem. Phys.* **2005**, *122*, 194319/1.

(10) Kohguchi, H.; Ohshima, Y.; Endo, Y. *Chem. Phys. Lett.* **1996**, *254*, 397.

(11) Tulej, M.; Meisinger, M.; Knopp, G.; Walser, A. M.; Gerber, T.; Radi, P. P. *J. Raman Spectrosc.* **2007**, *38*, 1022.

(12) Butenhoff, T.; Rohlfing, E. A. *J. Chem. Phys.* **1992**, *97*, 1595.

(13) Linnartz, H.; Motylewski, T.; Maier, J. P. *J. Chem. Phys.* **1998**, *109*, 3819.

(14) Motylewski, T.; Linnartz, H.; Vaizert, O.; Maier, J. P.; Galazutdinov, G. A.; Musaev, F. A.; Krelowski, J.; Walker, G. A. H.; Bohlender, D. A. *Astrophys. J.* **2000**, *531*, 312.

(15) Remy, J.; Biennier, L.; Salama, F. *Plasma Sources Sci. Technol.* **2003**, *12*, 295.

(16) Lovejoy, C. M.; Nesbitt, D. J. *Rev. Sci. Instrum.* **1987**, *58*, 807.

(17) Tanaka, K.; Sumiyoshi, Y.; Ohshima, Y.; Endo, Y.; Kawaguchi, K. *J. Chem. Phys.* **1997**, *107*, 2728.

(18) Dong, F.; Uy, D.; Davis, S.; Child, M.; Nesbitt, D. J. *J. Chem. Phys.* **2005**, *122*, 224301.

(19) Mazzotti, F. J.; Achkasova, E.; Chauhan, R.; Tulej, M.; Radi, P. P.; Maier, J. P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 136.

(20) Dreier, T.; Rakestraw, D. J. *Opt. Lett.* **1990**, *15*, 72.

(21) Ashfold, M. N. R.; Chandler, D. W.; Hayden, C. C.; McKay, R. I.; Heck, A. J. R. *Chem. Phys.* **1995**, *201*, 237.

(22) Scherer, J. J.; Paul, J. B.; O'Keefe, A.; Saykally, R. J. *Chem. Rev.* **1997**, *97*, 25.

(23) Field, R. W.; Hirota, E.; Maier, J. P.; Tsuchiya, S. Chapter 4. In *Nonlinear Spectroscopy for Molecular Structure Determination*; Blackwell Science: Oxford, U.K., 1998.

(24) Eichler, H. J.; Günter, P.; Pohl, D. W. *Laser-Induced Dynamic Gratings*; Springer-Verlag: New York, 1986; pp 84−146.

(25) Tulej, M.; Meisinger, M.; Knopp, G.; Walser, A. M.; Beaud, P.; Gerber, T.; Radi, P. P. *J. Raman Spectrosc.* **2006**, *37*, 376.

(26) Abrams, R. L.; Lind, R. C. *Opt. Lett.* **1978**, *2*, 94.

(27) Williams, S.; Zare, R. N.; Rahn, L. A. *J. Chem. Phys.* **1994**, *101*, 1072.

(28) Farrow, R. L.; Rakestraw, D. J. *Science* **1992**, *257*, 1894.

(29) Ewart, P.; O'Leary, S. V. *Opt. Lett.* **1986**, *11*, 279.

(30) Thomas, D.; Rakestraw, D. J. *Opt. Lett.* **1990**, *15*, 72.

(31) Radi, P. P.; Tulej, M.; Knopp, G.; Beaud, P.; Gerber, T. J. *J. Raman Spectrosc.* **2003**, *34*, 1037.

(32) Liu, C.-P.; Reid, S. A.; Lee, Y.-P. *J. Chem. Phys.* **2005**, *122*, 124313.

(33) Eckbreth, A. C. *Appl. Phys.* **1978**, *32*, 421.

(34) Butenhoff, T. J.; Rohlfing, E. A. *J. Chem. Phys.* **1993**, *98*, 5460.

(35) Farrow, R. L.; Rakestraw, D. J. *Science* **1992**, *257*, 1894.

(36) Hoshina, K.; Kohguchi, H.; Ohshima, Y.; Endo, Y. *J. Chem. Phys.* **1998**, *108*, 3465.

(37) Kuhn, R.; Maier, J. P.; Ochsner, M. *Mol. Phys.* **1986**, *59*, 441.

(38) McCormack, E. F.; Pratt, S. T.; Dehmer, P. M.; Dehmer, J. L. *Chem. Phys. Let.* **1993**, *11*, 147.

(39) Maier, J. P.; Thommen, F. *J. Chem. Phys.* **1980**, *73*, 5616.

(40) Helm, R. M.; Neuhauser, R.; Neusser, H. J. *Chem. Phys. Lett.* **1996**, *249*, 365.

(41) Williams, S.; Tobiason, J. D.; Dunlop, J. R.; Rohlfing, E. A. *J. Chem. Phys.* **1995**, *102*, 8342.

(42) Radi, P. P. Paul Scherrer Institut, 5232 Villigen PSI, private communication.

(43) Mueller, T.; Vaccaro, P. H. *Chem. Phys. Lett.* **1997**, *266*, 575.

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