



Methyl radical measurement by cavity ring-down spectroscopy

P. Zalicki ^a, Y. Ma ^a, R.N. Zare ^a, E.H. Wahl ^b, J.R. Dadamio ^b, T.G. Owano ^b,
C.H. Kruger ^b

^a *Department of Chemistry, Stanford University, Stanford, CA 94305, USA*

^b *Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA*

Received 29 December 1994

Abstract

Cavity ring-down spectroscopy has been used to measure the absorbance of methyl radicals near 216 nm. The methyl radicals are generated by a hot tungsten filament heated to 2300 K in a mixture of 0.5% CH₄ in H₂ slowly flowing through the reactor at 20 Torr total pressure. CH₃ absorbances are detected with a noise-equivalent sensitivity of two parts in 10⁵ using a narrow pencil of UV light 0.5 mm in diameter, which allows measurement of spatial profiles of CH₃ for column densities of 3 × 10¹² radicals/cm² (3 × 10¹² radicals/cm³ × 1 cm absorption pathlength).

The methyl radical is an important free radical present during the initial stages of hydrocarbon combustion. It is also believed to be a precursor for diamond growth by chemical vapor deposition. Therefore, interest exists in sensitive spectroscopic techniques for nonintrusive diagnostics of methyl radicals in various high-temperature environments such as plasmas, flames, discharges, etc. We report a new, highly sensitive measurement of methyl radicals based on cavity ring-down spectroscopy (CRDS) near 216 nm. Using CRDS, the CH₃ absorbance has been measured with submillimeter spatial resolution and with a noise-equivalent sensitivity of 25 ppm, corresponding, for absorption at 216.6 nm and gas temperature of 1600 K, to a column density of 3 × 10¹² methyl radicals/cm².

The first spectroscopic observation of the free methyl radical was made by Herzberg and Shoomsmith [1] in 1956, who measured the VUV absorption spectra of the CH₃ Rydberg series originating at 216 nm. Twenty-five years later, with the advent of

tunable infrared lasers, the CH₃ radical was detected by infrared absorption on the ν_2 vibrational transition near 16 μm [2], and on the ν_3 vibrational transition near 3 μm [3,4]. Nonlinear spectroscopic techniques have also been used to detect the Raman-active ν_1 infrared transitions [5,6]. In addition resonance-enhanced multiphoton ionization (REMPI) has allowed detection of methyl radicals by ionization from the electronic states excited with one or two UV photons [7–12]. Recently, one-photon threshold photoelectron spectroscopy has been successfully used by Blush et al. [13] to observe the methyl radical by ground-state ionization with 126 nm radiation.

Two complementary spectroscopic techniques most commonly used for diagnostics of the gas-phase methyl radical are 2 + 1 REMPI at 333.5 nm and UV absorption near 216 nm. REMPI has been used for the measurement of CH₃ present in a hot-filament reactor [14–16] and in the supersonic molecular beam [17]. This technique gives high sensitivity

and good spatial resolution but it provides only relative concentrations that need to be calibrated using other techniques. Also, application of REMPI to plasmas or other media containing free charges is of limited utility. Absorption techniques have the ability to measure absolute concentrations and can be applied for diagnostics of ionized gases. Methyl radicals have been measured by absorption spectroscopy on the 216 nm $B^2A_1-X^2A_2'$ transition (β_1-X in Herzberg's notation). Childs et al. [18] measured CH_3 radicals in a hot-filament reactor using single-pass absorption spectroscopy with an ultrastable xenon arc lamp. Later, Etzkorn et al. [19] determined absolute concentrations of CH_3 in a low-pressure methane–oxygen flame using multiple-pass laser absorption spectroscopy.

We have developed diagnostics for the methyl radical based on the cavity ring-down technique [20–25]. CRDS is a highly sensitive absorption spectroscopy that determines absorbance of the laser pulse passing across the absorbing sample. In a manner similar to single-pass laser absorption spectroscopy, this measurement is performed with two-dimensional spatial resolution; however, unlike the case of single-pass absorption spectroscopy, CRDS measures absorbances as low as 10^{-5} – 10^{-7} using a pulsed laser source with the usual 10%–20% pulse-to-pulse intensity jitter. This feature makes CRDS suitable for high-sensitivity measurements in the near UV spectral region where pulsed lasers are commonly used.

The CRDS technique, introduced by O'Keefe and Deacon [25] in 1988, is based on the measurement of the intensity of the light pulse trapped inside an optical cavity containing the absorbing sample. The pulse, generated by a nanosecond pulsed laser, is injected into the cavity through one of the mirrors and circulates inside the cavity as a stable transverse mode (without divergence). The intensity of the pulse as a function of time is monitored with a photodetector that collects the light transmitted through the second cavity mirror. When the cavity contains no absorbers, the intensity of light inside the cavity decays exponentially in time with a decay constant, the ring-down time τ_0 , given by the reflectivity \mathcal{R} of the cavity mirrors,

$$\tau_0 = t_r/2(1 - \mathcal{R}), \quad (1)$$

where t_r is the round-trip time for the light pulse inside the cavity. When the absorbing sample is placed inside the cavity and its absorption follows Beer's law [21], the pulse intensity also decays exponentially in time with a ring-down time τ which depends on both the reflectivity \mathcal{R} of the mirrors and the absorbance αl_s of the sample

$$\tau = t_r/[2(1 - \mathcal{R}) + \alpha l_s], \quad (2)$$

where α is the sample absorption coefficient, and l_s is the sample length. The quantity measured in CRDS is the sample absorbance αl_s , which is related to the measurements of τ_0 and τ by

$$\alpha l_s = \frac{t_r}{2} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right). \quad (3)$$

In our experiment, the decay times τ and τ_0 are determined from the real-time computer fit of the ring-down waveform to an exponential function.

For accurate absorbance measurements, the condition for Beer's law of absorption must be met, which implies that the absorption feature must be wider than the linewidth of the light inside the cavity. This condition is well fulfilled for the methyl radical absorption feature near 216 nm, which is a few nm wide. For accurate absorbance measurements, it is also important that the ground-state population of the absorber molecule is not significantly depleted by excitation during the time the laser pulse is circulating inside the optical cavity. We discuss this topic in the Appendix. In our experiment, for 216 nm light pulse of energy about 0.2 μ J and TEM_{00} mode radius $w = 250$ μ m, for mirrors reflectivity $\mathcal{R} = 0.991$ and effective transmittivity $\mathcal{T}_{\text{eff}} \approx 0.003$, and for CH_3 absorption cross section $\sigma < 10^{-17}$ $\text{cm}^2/\text{molecule}$ [26,27], the fraction of molecules excited by the laser pulse inside the cavity is less than 3×10^{-3} , which is sufficient for accurate CRDS measurements.

The schematic of our CRDS setup is shown in Fig. 1. An excimer-laser-pumped dye laser (Lambda-Physik) working with coumarin 440 was used as the pulse source. The pulses were 15 ns long with 0.18 cm^{-1} linewidth. After frequency doubling in a BBO crystal with an Inrad Autotracker, the 216 nm pulse was shaped with the system of pinholes and lenses to match approximately the TEM_{00} transverse mode of the optical cavity. The quasi-hemispherical optical

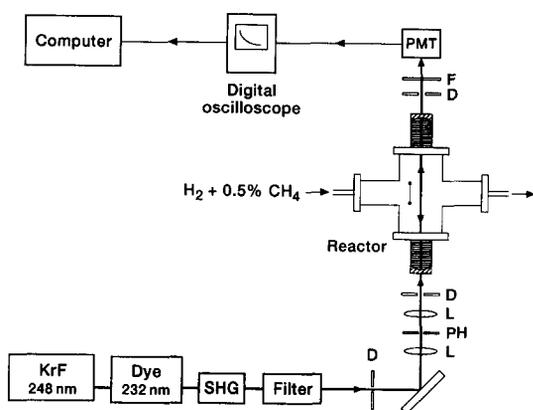


Fig. 1. Experimental setup for cavity ring-down spectroscopy of a hot-filament reactor: D = iris diaphragm, L = lens, PH = 50 μm pinhole, and F = spectral filter centered at 216 nm.

cavity was 53 cm long with the flat entrance mirror and the 2 m curvature concave back mirror. The mirrors were coated by Lightning Optical Corp. and reflected 99.1% at 216 nm, as determined directly by the ring-down time τ_0 of the empty cavity. The TEM₀₀ cavity mode has approximately a cylindrical form 0.5 mm in diameter.

Methyl radicals were generated in a hot-filament reactor filled with a 20 Torr mixture of hydrogen with 0.5% of methane flowing at 100 sccm rate. The filament was tungsten, 19 mm long and 200 μm in diameter, heated resistively with a dc current to 2300 K. The filament temperature was measured with a disappearance pyrometer (Pyro Micro-Optical Pyrometer, The Pyrometer Instrument Co., Inc., Northvale, NJ, USA).

The ring-down cavity was attached to the hot-filament reactor by means of flexible bellows in such a way that the laser pulse circulated inside the cavity parallel to the filament. The light transmitted through the back mirror of the cavity was collected by a photomultiplier (PMT) and the PMT signal as a function of time was recorded on an HP 54510A digitizing oscilloscope with 2 ns temporal resolution. To assure that the pulse circulated along the same path inside the cavity, a small diaphragm ≈ 1 mm in diameter was placed on the light path between the back mirror of the cavity and the PMT. The light emerging from the cavity passes undisturbed through the diaphragm, indicating good alignment of the cavity.

The ring-down waveforms digitized on the oscilloscope were transferred to a PC computer, averaged, and the ring-down time τ was obtained from a real-time computer fit. We used the standard fitting procedure where the natural logarithm of the ring-down waveform is fit to a straight line with a y^2 weighting, where y is the waveform amplitude. This weighting was chosen because the variance of the amplitude y is approximately equal to y^2 times the variance of $\ln y$. The CH_3 absorbance is obtained with the help of Eq. (3) in which the ring-down time τ is measured at the distance of 4.5 mm from the filament, and the ring-down time τ_0 is measured at the distance of 24 mm from the filament, where no methyl absorption is observed.

A typical ring-down waveform is shown in Fig. 2. It is 1 μs long and includes an initial rise period, that is completed after the pulse entered the cavity, and a subsequent ring-down decay in which the ring-down time τ_0 is about 190 ns. The initial part of the decay is not exactly exponential, probably caused by transients in the detection system. This part of the decay was excluded from the fit, as shown in Fig. 2.

Special attention was paid to the optimization of the sensitivity of the measurement. The sensitivity of CRDS is limited by two factors: the reflectivity \mathcal{R} of the mirrors and the accuracy in the determination of τ . By combining Eq. (3) with Eqs. (1) and (2) we obtain

$$(\alpha l_s)_{\min} = (1 - \mathcal{R}) \left(\frac{\Delta\tau}{\tau} \right)_{\min} \quad (4)$$

Best sensitivities of CRDS can be achieved for an optical cavity formed with highly reflective mirrors for which the reflection loss coefficient $(1 - \mathcal{R})$ is minimized. At visible wavelengths the mirror reflectivities range from 99.99% (see for example Ref. [28]) up to 99.99984% [29], whereas at UV wavelengths between 300 and 200 nm best reflectivities are in the range of 99.5% to 99% [24,30]. For the given set of mirrors forming an optical cavity, the reflectivity \mathcal{R} is fixed, and the sensitivity of CRDS can be maximized by increasing the τ confidence level. This increase can be achieved by minimizing the standard deviation σ_τ of the ring-down time τ measured on a single laser pulse, by averaging the ring-down waveforms before τ is fit, and by averaging the τ values. For our CRDS system, the standard

deviation σ_r was approximately 2.7% of the τ value. To increase the τ confidence level, the ring-down waveforms were transferred from the oscilloscope to the computer, averaged in groups of 32 in a 32-bit computer memory, and then fit. The CH_3 absorbance was determined as an average of 8 τ values (256 laser shots), which was achieved in about 20 s and gave the noise-equivalent sensitivity of $2\sigma_{\alpha l_s} = 25$ ppm. Fig. 3 presents the observed dependence of the standard deviation of the noise on the number of averaged ring-down waveforms.

The CRDS spectrum of CH_3 near 216 nm is shown in Fig. 4. The absorbance was measured at a 4.5 mm distance from the filament at the filament temperature of 2300 K. The spectrum features two broad absorption peaks characteristic of the CH_3 β_1 -X electronic transition. The estimated concentration of CH_3 in the reactor is 5×10^{13} radicals/ cm^3 ,

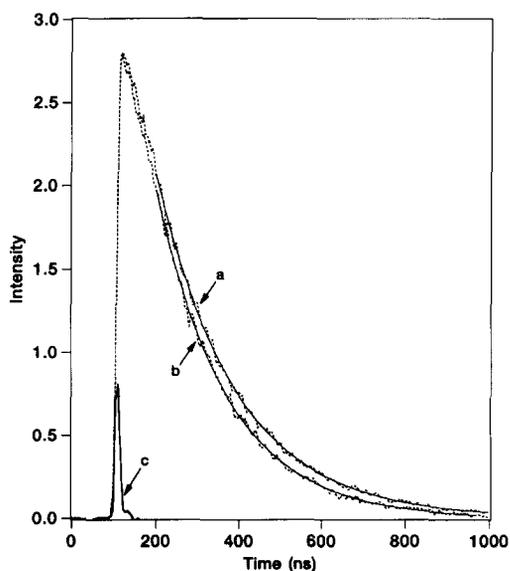


Fig. 2. Ring-down decay waveforms observed at 216.6 nm for (a) absorbance $\alpha l_s = 0$; (b) absorbance $\alpha l_s = 0.0012$. Waveform (c) presents a profile of the laser pulse observed for a misaligned ring-down cavity. The waveforms are averaged over 32 laser shots in the computer memory for more accurate determination of the ring-down time τ . The solid line (exponential) marks that part of the waveform that was used to determine τ from the fit. Note the difference in the intensity of the PMT signal for the laser pulse transmitted through the cavity aligned and the cavity misaligned. The change in the cavity transmittivity with degree of alignment is caused by interference inside the cavity for the pulse length t_p about 10 times longer than the cavity round-trip time t_r .

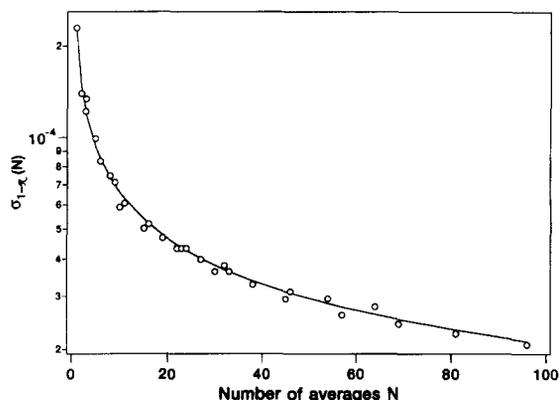


Fig. 3. Standard deviation of the reflection loss $1 - \mathcal{R}$ as a function of the number of averaged ring-down waveforms N , and the fit to $2.08 \times 10^{-4} / N^{1/2}$. The dependence was obtained from the sample of 10^4 ring-down waveforms collected for the cavity containing no absorber. Therefore, the quantity measured is the reflection loss $1 - \mathcal{R}$. The initial standard deviation σ_1 is approximately 2.7% of the mean $1 - \mathcal{R}$ value and decreases as $N^{1/2}$, which indicates that the noise in the $1 - \mathcal{R}$ measurement is random.

based on the absorbance value at 216.6 nm, a path-length of 3 cm, and an absorption cross section of $\sigma = 0.8 \times 10^{-17}$ $\text{cm}^2/\text{molecule}$ [27], assuming a temperature of 1600 K [31].

In Fig. 4, we compare the CRDS spectrum of CH_3 to the analogous spectrum of CH_3 obtained by Etzkorn et al. [19] in a low-pressure flame by multiple-pass laser absorption spectroscopy. The methyl radical absorption features shown in both spectra are similar; however, the CH_3 column density of about 2×10^{15} molecules/ cm^2 (absorbance 0.027 at 216.6 nm and 660 K gas temperature) is measured by multiple-pass laser absorption spectroscopy, whereas thirteen times smaller CH_3 column density (absorbance 0.0012 at 216.6 nm wavelength and 1600 K gas temperature) is measured with CRDS. In both cases similar, pulsed dye lasers are used as light sources.

We have also found that acetylene is generated in our hot-filament reactor. Because acetylene is a stable molecule, it is uniformly distributed inside the reactor, and its absorption measurement is facilitated by the long pathlength which is equal to the cavity length of 53 cm. The acetylene was measured at a distance of 24 mm from the filament. The absorbance of the acetylene $\tilde{A}^1A_u - \tilde{X}^1\Sigma_g^+, V_0^4K_0^1$ rovi-

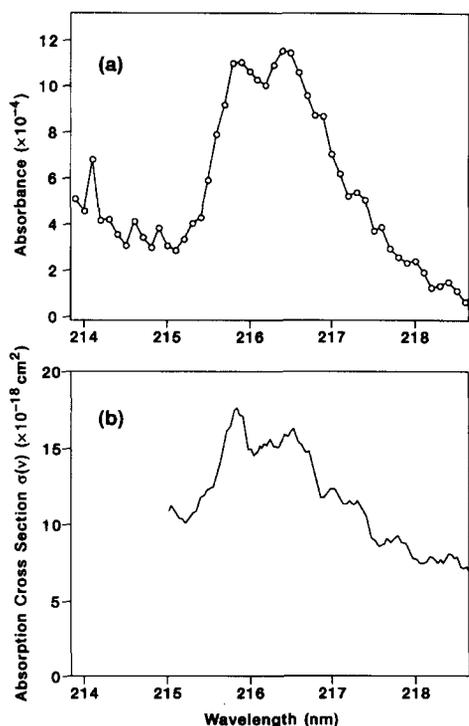


Fig. 4. The absorbance spectrum of the $\text{CH}_3 \beta_1\text{-X}$ electronic transition near 216 nm measured by (a) CRDS, for CH_3 column density of 1.5×10^{14} radicals/ cm^2 (this work), (b) multiple-pass laser absorption spectroscopy, for CH_3 column density of 2×10^{15} radicals/ cm^2 which is equivalent to absorbance 0.027 at 216.5 nm and 660 K gas temperature (based on Figs. 2 and 3 in Ref. [19]). The CRDS spectrum was measured with 1 Å spectral resolution, 4.5 mm from the tungsten filament. Values of τ_0 were determined at a distance of 24 mm from the filament for the initial and final wavelength shown in this figure. The absorption features between 214 and 215 nm are caused by acetylene absorption lines that are less than 0.1 Å wide.

brational transitions near 216.1 nm was about 2×10^{-4} .

The CH_3 absorption feature near 216 nm overlaps with the observed acetylene lines. Because acetylene absorption bands do not form a continuum, it is possible to isolate spectrally the measurement of methyl from the measurement of acetylene. No acetylene lines were observed near 216.6 nm, where the methyl radical cross-section data are available [26,27].

On the basis of our observations we conclude that the CRDS technique can be used for quantitative diagnostic of methyl radicals with high sensitivity.

This technique measures CH_3 absorbance near 216 nm with a noise-equivalent sensitivity on the order of 25 ppm (corresponding, for absorption at 216.6 nm and a gas temperature of 1600 K, to a column density of 3×10^{12} methyl radicals/ cm^2). We used CRDS for the measurement of methyl radicals generated in a hot-filament reactor; however, the CRDS technique is feasible for quantitative measurements of CH_3 in other high-temperature media including flames, plasmas, discharges, etc. Because methyl radicals are found in a variety of hot-gas environments, CRDS should possess wide applicability as a CH_3 diagnostic.

This work was supported under the auspices of the US Department of Energy, grants DE-FG03-92ER14304 and DE-FG03-88ER13957.

Appendix

We estimate the fraction η of the absorber molecules excited by the laser pulse inside the optical cavity assuming that the processes of diffusion and relaxation are frozen during the ring-down decay and, therefore, the molecules become optically inactive after excitation. Under these conditions, the number of molecules excited inside the cavity is equal to the number of absorbed photons. The largest fraction of molecules is excited near the axis of the cavity TEM_{00} mode, where the intensity of light in the cavity reaches a maximum. The number of photons propagating along this axis within the transverse area dS is given by $(N/\pi w^2) \mathcal{F}_{\text{eff}} dS$, where N is the number of photons within the laser pulse (given by the ratio of the pulse energy to the photon energy $\hbar c/\lambda$), w is the radius of the TEM_{00} cavity mode, and \mathcal{F}_{eff} is the effective transmittivity of the cavity mirrors (\mathcal{F}_{eff} is larger than transmittivity \mathcal{F} of the mirror coating because of the cavity étalon effect for the pulse length longer than the cavity round-trip length t_r [21]). Only a fraction $\alpha l_s/(1 - \mathcal{R} + \alpha l_s)$ of the photons inside the cavity becomes absorbed. Therefore, the fraction of molecules excited inside the cavity is given by

$$\eta = \frac{N}{\pi w^2} \mathcal{F}_{\text{eff}} \frac{\alpha l_s}{1 - \mathcal{R} + \alpha l_s} dS/nl_s dS. \quad (\text{A.1})$$

In Eq. (A.1), $nl_s dS$ is the total number of molecules in the excitation volume. By substituting for the concentration n the ratio of the absorption coefficient α to the absorption cross section σ , and by neglecting the factor αl_s in the denominator of Eq. (A.1), which is a good approximation for the usual case of $(1 - \mathcal{R}) > \alpha l_s$, we obtain

$$\eta \leq \frac{N}{\pi w^2} \frac{\mathcal{F}_{\text{eff}}}{1 - \mathcal{R}} \sigma. \quad (\text{A.2})$$

In Eq. (A.2), we expressed the fraction of molecules excited inside the cavity by equating it to the probability of the excitation process. Consequently, η depends on the absorption cross section σ rather than on the absorber concentration n . To match the experimental requirements, η should be on the order of 0.01% or less. This limiting value can be achieved by an appropriate decrease in the laser pulse energy $N\hbar c/\lambda$ and an increase in the radius w of the cavity transverse mode.

References

- [1] G. Herzberg and J. Shoosmith, *Can. J. Phys.* 34 (1956) 523.
- [2] C. Yamada, E. Hirota and K. Kawaguchi *J. Chem. Phys.* 75 (1981) 5256.
- [3] T. Amano, P.F. Bernath and C. Yamada, *Nature* 296 (1982) 327.
- [4] T. Amano, P.F. Bernath, C. Yamada, Y. Endo and E. Hirota, *J. Chem. Phys.* 77 (1982) 5284.
- [5] P.L. Holt, K.E. McCurdy, R.B. Weisman, J.S. Abrams and P.S. Engel, *J. Chem. Phys.* 81 (1984) 3349.
- [6] P.B. Kelly and S.G. Westre, *Chem. Phys. Letters* 151 (1988) 253.
- [7] T.G. DiGiuseppe, J.W. Hudgens and M.C. Lin, *Chem. Phys. Letters* 82 (1981) 267.
- [8] J. Danon, H. Zacharias, H. Rottke and K.H. Welge, *J. Chem. Phys.* 76 (1982) 2399.
- [9] T.G. DiGiuseppe, J.W. Hudgens and M.C. Lin, *J. Phys. Chem.* 86 (1982) 36.
- [10] T.G. DiGiuseppe, J.W. Hudgens and M.C. Lin, *J. Chem. Phys.* 76 (1982) 3338.
- [11] B.H. Rockney and E.R. Grant, *J. Chem. Phys.* 77 (1982) 4257.
- [12] J.W. Hudgens, T.G. DiGiuseppe and M.C. Lin, *J. Chem. Phys.* 79 (1983) 571.
- [13] J.A. Blush, P. Chen, R.T. Wiedmann and M.G. White, *J. Chem. Phys.* 98 (1993) 3557.
- [14] E. Villa, J.A. Dagata, J. Horwitz, D. Squire and M.C. Lin, *J. Vacuum Sci. Technol. A* 8 (1990) 3237.
- [15] F.G. Celii and J.E. Butler, *J. Appl. Phys.* 71 (1992) 2877.
- [16] E.J. Corat and D.G. Goodwin, *J. Appl. Phys.* 74 (1993) 2021.
- [17] S.S. Lee, D.W. Minsek, D.I. Vestyck and P. Chen, *Science* 263 (1994) 1596.
- [18] M.A. Childs, K.L. Menningen, P. Chevako, N.W. Spellmeyer, L.W. Anderson and J.E. Lawler, *Phys. Letters A* 171 (1992) 87.
- [19] T. Etzkorn, J. Fitzer, S. Muris and J. Wolfrum, *Chem. Phys. Letters* 208 (1993) 307.
- [20] D. Romanini and K.K. Lehmann, *J. Chem. Phys.* 99 (1993) 6287.
- [21] P. Zalicki and R.N. Zare, *J. Chem. Phys.* 102 (1995), in press.
- [22] A. O'Keefe, J.J. Scherer, A.L. Cooksy, R. Sheeks, J. Heath and R.J. Saykally, *Chem. Phys. Letters* 172 (1990) 214.
- [23] T. Yu and M.C. Lin, *J. Am. Chem. Soc.* 115 (1993) 4371.
- [24] G. Meijer, M.G.H. Boogaarts, R.T. Jongma, D.H. Parker and A.M. Wodtke, *Chem. Phys. Letters* 217 (1994) 112.
- [25] A. O'Keefe and D.A.G. Deacon, *Rev. Sci. Instr.* 59 (1988) 2544.
- [26] D.F. Davidson, A.Y. Chang, M.D.D. Rosa and R.K. Hanson, *J. Quant. Spectry. Radiative Transfer* 49 (1993) 559.
- [27] D.F. Davidson, M.D.D. Rosa, E.J. Chang and R.K. Hanson, submitted for publication.
- [28] The 1994 Newport Catalog (Newport Corp., Irvine, CA, 1994) p. 23.
- [29] G. Rempe, R.J. Thompson, H.J. Kimble and R. Lalezari, *Opt. Letters* 17 (1991) 363.
- [30] R.T. Jongma, M.G.H. Boogaarts and G. Meijer, *J. Mol. Spectry.* 165 (1994) 303.
- [31] M. Chenevier, J.C. Cubertafon, A. Campargue and J.P. Booth, *Diamond Relat. Mater.* 3 (1994) 587.