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Richard Engeln, Gerard Meijer

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# A Fourier transform cavity ring down spectrometer

Richard Engeln<sup>a)</sup> and Gerard Meijer

Department of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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We present a pulsed multiplex absorption spectrometer in which the sensitivity of the cavity ring down absorption detection technique is combined with the multiplex advantage of a Fourier Transform spectrometer. A description of the Fourier transform cavity ring down (CRD) spectrometer—substantiated with first experimental results on the atmospheric band of molecular oxygen—is given. It is shown that as in the case of *normal* CRD spectroscopy, the measurement is independent of light intensity fluctuations provided the spectral intensity distribution of the light source is known and is constant during the measurement. © 1996 American Institute of Physics. [S0034-6748(96)01407-4]

## I. INTRODUCTION

In 1988, O'Keefe and Deacon<sup>1</sup> demonstrated a new direct absorption spectroscopic technique that can be performed with a pulsed light source and that has a significantly higher sensitivity than obtainable in *conventional* absorption spectroscopy. This so-called cavity ring down (CRD) technique is based upon the measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined in a closed optical cavity with a high Q factor.<sup>1</sup> The advantage over normal absorption spectroscopy results from (i) the intrinsic insensitivity of the CRD technique to light source intensity fluctuations, and (ii) the extremely long effective pathlengths (many kilometers) that can be realized in stable optical cavities.

Since the technique is based on a pulsed measurement, it can be used in combination with pulsed molecular beams,<sup>2–4</sup> and it can also be used to study dynamical processes via time-resolved absorption measurements.<sup>5</sup> The high sensitivity of the technique is explicitly shown by Romanini and Lehmann in their study of the overtone and combination bands of the molecule HCN in the visible part of the spectrum.<sup>6</sup> They report absorption spectra with a noise equivalent absorption detection limit in the  $10^{-10}$  cm<sup>-1</sup> range, using mirrors with reflectivity losses below 100 ppm, i.e., with a reflectivity  $R \geq 0.9999$ .

CRD spectroscopy can be performed with a high spectral resolution and a good sensitivity even in relatively short cavities, and has been applied in the UV part of the spectrum,<sup>7,8</sup> as well as in the IR spectral region.<sup>9</sup> It has been demonstrated that especially in the near-UV, CRD spectroscopy holds great promise for trace gas detection.<sup>10</sup> Around 250 nm where no mirrors with a reflectivity better than  $R=0.997$  are available yet, absorption down to  $10^{-7}$  cm<sup>-1</sup> is still readily detected.<sup>11</sup> Potential problems associated with the mode structure of the cavities<sup>1,12,13</sup> can be easily circumvented by using a stable optical cavity with a near-continuum mode structure.<sup>7</sup>

In most of the aforementioned studies, it is assumed that the linewidth of the light source can be neglected compared

to the width of the molecular absorption. It has been shown, however, that if this assumption is no longer valid, one can still extract the correct absorption coefficient from the measured transients, provided the spectral intensity distribution of the light source is known.<sup>10,13</sup> In addition, it should be noted that a narrow band pulsed laser is not necessarily needed to perform a CRD experiment. A polychromatic light source might be used to extract the spectral information after spectrally dispersing the light exiting the cavity. For this, the temporal shape of the ring down transient for a specific frequency (interval) has to be recorded and analyzed. A monochromator with suitable detector or a time-resolved optical multichannel analyzer could, for instance, be used for this.

In this article, we present a spectrometer that uses a polychromatic pulsed light source which is coupled into an optical cavity. The light exiting the cavity is coupled into a Michelson interferometer. The time dependence of the ring down transient per frequency interval is found after Fourier transformation of the measured time dependence of the (spectrally integrated) ring down transients recorded at well-defined interferometer arm length differences. In this so-called Fourier transform-cavity ring down (FT-CRD) spectrometer, the multiplex advantage of FT spectrometers is combined with the demonstrated sensitivity of the CRD absorption detection technique. We detail the operation principle of this FT-CRD spectrometer, show experimental results and outline the advantages over the standard FT-absorption spectrometers.

## II. THEORETICAL DESCRIPTION

In a typical CRD experiment, a short light pulse is coupled into a stable optical cavity formed by two highly reflecting plano-concave mirrors. The fraction of light entering the cavity on one side *rings* back and forth many times between the two mirrors. The time behavior of the light intensity inside the cavity  $I_{\text{CRD}}(t)$  can be monitored by the small fraction of light that is transmitted through the other mirror. If the only loss factor in the cavity is the reflectivity loss of the mirrors, one can show that the light intensity inside the cavity decays exponentially in time with a decay constant  $\tau_0$ , the *ring down time*, given by:

<sup>a)</sup>Electronic mail: richarde@sci.kun.nl.

$$\tau_0 = \frac{d}{c(|\ln R|)} \quad (1)$$

Here  $d$  is the optical path length between the mirrors,  $c$  is the speed of light, and  $R$  is the reflectivity of the mirrors. If  $R$  is close to unity, the approximation  $\tau_0 = d/c(1-R)$  can be made.

If there is additional loss inside the cavity due to the presence of absorbing and light scattering species, the light intensity inside the cavity will still decay exponentially in time provided the absorption follows Beer's law. It can be shown that in this case, the ring-down transient is proportional to:

$$I_{\text{CRD}}(t) \propto \int_0^\infty I(\nu) \exp\left(-\frac{t}{\tau(\nu)}\right) d\nu, \quad (2)$$

where  $I(\nu)$  is the spectral distribution of the light that is coupled into the cavity and where  $\tau(\nu)$  is given by:

$$\tau(\nu) = \frac{d}{c(|\ln R_\nu| + \sum_i \sigma_i(\nu) \int_0^d N_i(x) dx)} \quad (3)$$

and the sum is over all light scattering and absorbing species with frequency dependent cross sections  $\sigma_i(\nu)$  and a line-integrated number density  $\int_0^d N_i(x) dx$ . The product of the frequency dependent absorption cross section with the number density  $N_i(x)$  is commonly expressed as the absorption coefficient  $\kappa_i(\nu, x)$ . In many cases, the line-integrated number density will be constant in time, but even if there is a time dependence of  $\int_0^d N_i(x) dx$ , this can be extracted from the ring down transient and dynamical processes can be studied in this way.<sup>5</sup> The losses due to Rayleigh or Mie scattering can be considered as frequency independent over the narrow frequency range one is usually interested in. Since this is also true for the reflectivity of the mirrors, one can incorporate these loss factors by substituting for  $R_\nu$  an effective loss factor  $R_{\text{eff}}$ . From Eq. (3), it is clear that the parameter  $\tau(\nu)$ —which is deduced from the measured transient—is independent of the intensity of the light pulse coupled into the cavity but only depends on the properties of the cavity and of the absorbing species.

It is evident from Eqs. (2) and (3) that the cavity ring down transient is only a single exponentially decaying curve if the width of the radiation that is coupled into the cavity is much smaller than the width of the absorption features. It has been shown<sup>10,13</sup> that although the CRD technique loses its linearity with respect to increasing absorption when the line-width of the light source can no longer be neglected with respect to the absorption features, one can still accurately determine the absorption cross section, provided the spectral intensity distribution of the light source is known.

If a broad band light source is used in combination with a FT spectrometer, the intensity of the light that passes through the interferometer is recorded as a function of the optical path length difference  $\Delta$ , between the two arms of the interferometer;

$$I(\Delta) = \int_0^\infty I(\nu) \cos^2(\pi \nu \Delta) d\nu. \quad (4)$$

The intensity as function of  $\nu$  is obtained by Fourier transformation of  $I(\Delta)$ , i.e.,

$$I(\nu) = \int_{-\infty}^\infty I(\Delta) \exp(i2\pi \nu \Delta) d\Delta. \quad (5)$$

Standard FT-absorption spectrometers operate according to this principle.

To detect the frequency and time dependence of a certain process simultaneously—to study the spectral and temporal behavior of laser induced molecular fluorescence for instance—time-resolved Fourier transform spectroscopy can be performed. In this case, one detects the temporal dependence of the spectral integrated intensity as a function of  $\Delta$ , i.e., one measures

$$I(\Delta, t) = \int_0^\infty I(\nu, t) \cos^2(\pi \nu \Delta) d\nu. \quad (6)$$

The Fourier transformation of this expression yields  $I(\nu, t)$ : the time dependence of the intensity at frequency  $\nu$ . Various suppliers of FT spectrometers have currently implemented the necessary hardware and software to move the mirrors of the interferometer in such a way that time-resolved FT-spectroscopy can be performed.<sup>14,15</sup>

In the FT-CRD spectrometer presented, a time-resolved FT-spectroscopic measurement of the broad band light exiting a ring down cavity is performed. In this case, the measured quantity is  $I(\Delta, t)$  which is generally not an exponentially decaying function of time. After Fourier transformation of  $I(\Delta, t)$ , the ring down transient per frequency (interval)  $I(\nu, t)$  is obtained. This can be written as

$$I(\nu, t) = I(\nu, 0) \exp[-t/\tau(\nu)] \quad (7)$$

and  $\tau(\nu)$ , and thereby  $\kappa(\nu)$ , can be determined over the complete spectral range covered by the light source.

In a standard CRD experiment, in which a narrow-band pulsed laser is used, the absorption information is deduced from the temporal shape of the ring down transient recorded at a certain frequency and is independent of the absolute intensity of the ring down signal. It suffices, therefore, to record normalized ring-down transients at each laser frequency. In the FT-CRD spectrometer, the absorption information is deduced from the temporal shape of the ring-down transient that is now recorded as a function of the path-length difference  $\Delta$  in the interferometer. Also, in this case, it is sufficient to only record normalized transients. These transients  $I_{\text{norm}}(\Delta, t)$ —normalized to have the same maximum value at  $t=0$  for all values of  $\Delta$ —can be written as

$$I(\Delta, t) = I_{\text{norm}}(\Delta, t) I(\Delta, 0). \quad (8)$$

The Fourier transform of the left-hand side of this expression yields the required  $I(\nu, t)$  from which the absorption spectrum can be deduced. According to the convolution theorem of Fourier analysis, the Fourier transform of a product of two functions is identical to the convolution of their individual Fourier transforms. This implies that  $I(\nu, t)$  can also be obtained by taking the convolution of the Fourier transform of the normalized interferograms with the Fourier transform of  $I(\Delta, 0)$ . The latter is nothing else than the spectral intensity distribution of the light at the time it enters the ring down

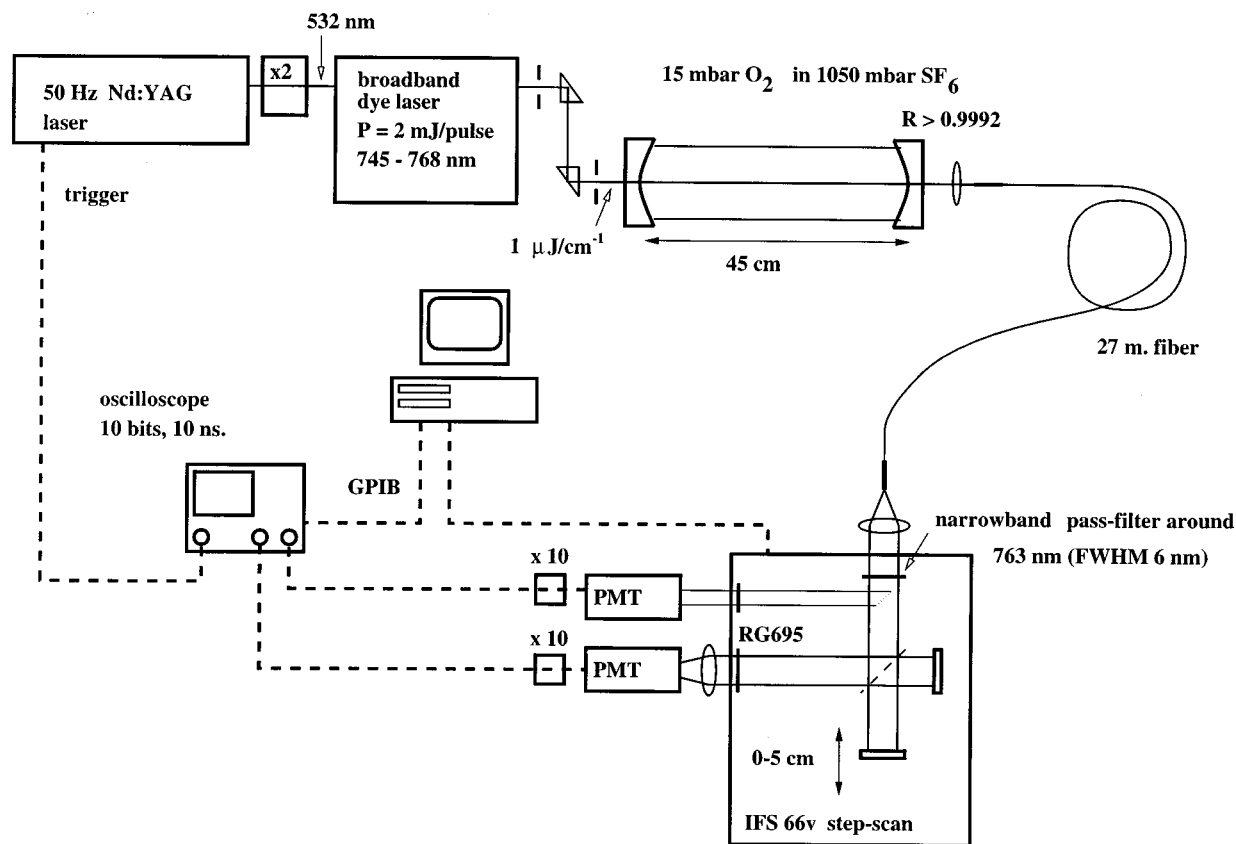


FIG. 1. Schematic view of the experimental setup. Broadband pulsed laser radiation is coupled into an optically stable ring down cavity. The light exiting the cavity is transported via an optical fiber to a Bruker IFS 66v FT spectrometer, with step-scan option. Ring-down transients are recorded as a function of the optical path length difference between the arms of the interferometer on a fast, high resolution digital oscilloscope.

cavity. So, provided the spectral intensity distribution of the light source is known and is constant during the measurements, a measurement of  $I_{\text{norm}}(\Delta, t)$ —an intensity independent measurement—suffices to obtain the absorption spectrum. It is explicitly noted that the requirement on the spectral intensity distribution of the light source used in the FT-CRD spectrometer is not at all a restriction compared to that in the standard CRD experiment. Also in the standard CRD experiment, the spectral intensity distribution has to be known and has to be constant during the measurement to be able to extract accurate absolute absorption values.<sup>10,13</sup>

### III. EXPERIMENT

A schematic representation of the experimental setup is depicted in Fig. 1. As a light source, we use a Spectra Physics PDL 2 dye laser, pumped by a 50 Hz frequency doubled Nd:YAG laser (Spectra Physics GCR 190/50). The Nd:YAG laser produces 250 mJ at 532 nm of which only 20 mJ is used to pump the oscillator stage of the dye laser. The dye laser is operated on a mixture of styryl 8 and styryl 9. With the grating in the zeroth order, a 5 ns light pulse with an energy of 2 mJ and a spectral width of about  $400 \text{ cm}^{-1}$  is produced. The spectral intensity distribution of this broadband light source will fluctuate from pulse-to-pulse due to mode competition in the oscillator but the overall spectral shape is expected to remain sufficiently constant during the course of the measurements. After passing through two pin-

holes, a light pulse with a spectral energy density of approximately  $1 \mu\text{J}/\text{cm}^{-1}$  is directed toward the ring down cavity. No mode matching is performed to allow a near continuum of modes to build up in the cavity.<sup>7</sup>

The experimental details for the ring down cavity do not differ from the *standard* setup we have been using.<sup>10</sup> In short, a cavity is formed by two identical plano-concave mirrors with a 25 mm diam and a radius of curvature of -25 cm placed slightly over 45 cm apart. The reflectivity coatings are optimized for  $\lambda = 750 \text{ nm}$ , but still have an effective reflection coefficient of  $R_{\text{eff}} \approx 0.9992$  around 763 nm, the wavelength used in the experiments.

The light pulse of the dye laser is coupled into the cavity from one side, and the light that leaks out through the mirror on the other side is focused with a microscope objective onto a fiber. In order to ensure that all transverse modes are detected with equal probability, the microscope objective is placed as close as possible to the out coupling mirror. The fiber—a multimode fiber with a diameter of  $200 \mu\text{m}$ —is mounted together with the microscope objective in a fiber coupler, which allows for fine tuning of the focus onto the fiber. The fiber guides the transmitted light to the FT-spectrometer (Bruker IFS 66v with step-scan option). A second fiber coupler is used to align the beam to the entrance port of the interferometer. The fine adjustment possibilities of the fiber coupler make it possible to create a parallel beam

which is of importance to obtain the desired accuracy and resolution with the FT spectrometer.

Before the light enters the interferometer, it passes through an interference filter that transmits a frequency band of about  $200\text{ cm}^{-1}$ , centered around  $13\,100\text{ cm}^{-1}$ . Part of the transmitted light is split off to a photomultiplier tube (PMT) for intensity calibration. It has been shown that pulse-to-pulse normalization improves the signal-to-noise (SNR) ratio in time-resolved FT experiments.<sup>16</sup> We pointed out before and will explicitly demonstrate later that this normalization is not required if only the temporal shape of the signal as a function of frequency is needed. Behind the interferometer the light is measured with a second PMT. In front of both PMTs two 2 mm thick high pass filters are placed, to sufficiently attenuate residual HeNe-laser light which is used as an internal reference signal in the interferometer. The interferometer is operated in the so-called *step-scan* mode, i.e., the movable mirror on the 5 cm long arm is moved to and fixed at a predefined position. The signals of both PMTs are amplified 10 times and measured with a fast (10 ns) and high resolution (10 bit) digital oscilloscope (LeCroy 9430). At every mirror position some 100 transients, every transient recorded over  $8\text{ }\mu\text{s}$ , are summed on the 16 bits onboard memory of the oscilloscope and read out by a PC via a GPIB interface connection. One measurement consists of the recording of transients  $I(\Delta, t)$  at typically 3000 mirror positions  $\Delta$ . At the end of the measurement, the data are rearranged such that arrays recorded at identical time points but at different mirror positions are formed. Thus full interferograms—measured at a specific time point—are obtained. These interferograms are Fourier transformed to obtain the spectral intensity distribution at this time point. This process is repeated for every time point at which the transients are recorded.<sup>14</sup> As the digital oscilloscope digitizes the signal every 10 ns, many spectra are generated. The data points belonging to the same frequency in the different spectra, are fitted to an exponentially decaying function of time. From the resulting decay time as a function of frequency, the absorption spectrum is extracted.

Since the data reduction can only start after having recorded the transients at all mirror positions, a large amount of data has to be stored during the measurement. To reduce this amount of data, every transient measured at a certain mirror position is cut into pieces of 100 ns, i.e., 10 data points are summed, and the averaged baseline—determined from 200 data points prior to the start of the transient—is subtracted. In this way, every transient is represented by 60 data points. Still 0.4 Mb of data had to be stored for the measurement of the spectrum of the (0,0) band of the  $\text{O}_2$   $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$  transition that is shown in the next section.

#### IV. RESULTS AND DISCUSSION

To illustrate the operation principle of the FT-CRD spectrometer, we performed an experiment using a light pulse with a spectral width: full width at half maximum (FWHM) of  $1.1\text{ cm}^{-1}$ . This light is obtained by operating the grating of the pulsed dye laser in first order. The center frequency of the laser pulse is chosen to coincide with the  $^P P_2(9)$  line of

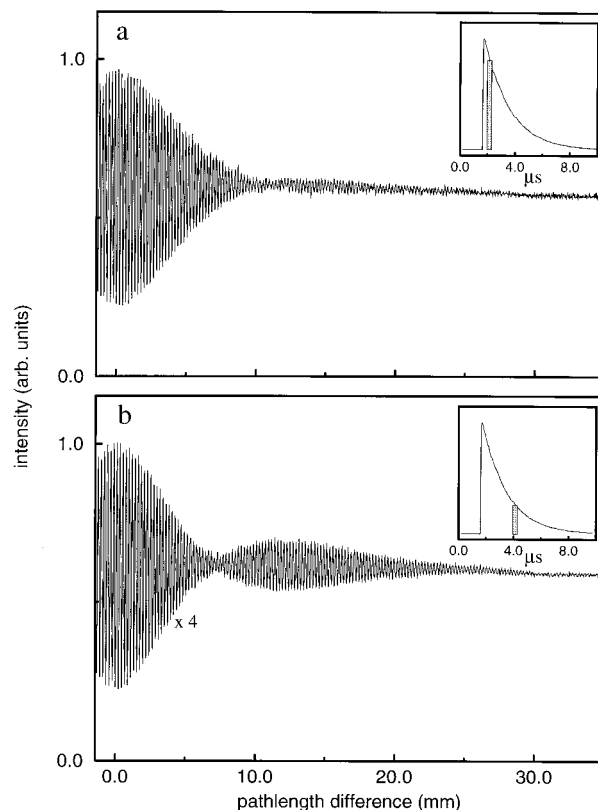


FIG. 2. Interferograms taken at the beginning of the ring down transient (a) and  $2\text{ }\mu\text{s}$  later (b). The inset shows the ring down transient and the shaded area indicates which part of the transient is used to record the interferograms. A narrow-band light source centered on top of an oxygen absorption line is used.

the oxygen  $b^1\Sigma_g^+, v'=0 \leftarrow X^3\Sigma_g^-, v''=0$  transition at  $13\,091.7\text{ cm}^{-1}$ .<sup>17</sup> The ring down transients, summed over 25 laser pulses, are measured as a function of the optical path length difference between the two arms of the interferometer. In Figs. 2(a) and 2(b), interferograms recorded during a 100 ns time interval at the beginning of the ring-down transient and  $2\text{ }\mu\text{s}$  later are shown, respectively. In the inset in Figs. 2(a) and 2(b) the ring-down transient, as well as the part of the transient that is selected for the measurement of the interferograms, is indicated. As described in the previous section, a separate PMT is used to measure the spectrally integrated intensity of the light entering the FT spectrometer. The interferograms presented in Figs. 2(a) and 2(b) are corrected for intensity fluctuations using the signal of this PMT.

The spectra shown in Figs. 3(a) and 3(b) are obtained via Fourier transformation of the interferograms presented in Figs. 2(a) and 2(b), respectively. The spectrum in Fig. 3(a) shows the spectral intensity distribution of the light pulse at the beginning of the ring down transient. This is the spectral intensity distribution as determined by the pulsed laser, in combination with the weak (but already visible) averaged absorption that occurs during the first 100 ns (30 meter path length). After  $2\text{ }\mu\text{s}$ , i.e., after 600 meter extra path length, the spectrum as presented in Fig. 3(b) is obtained in which the  $\text{O}_2$  absorption line is readily recognized. It is evident from these two spectra, a two-point measurement of the lifetime,

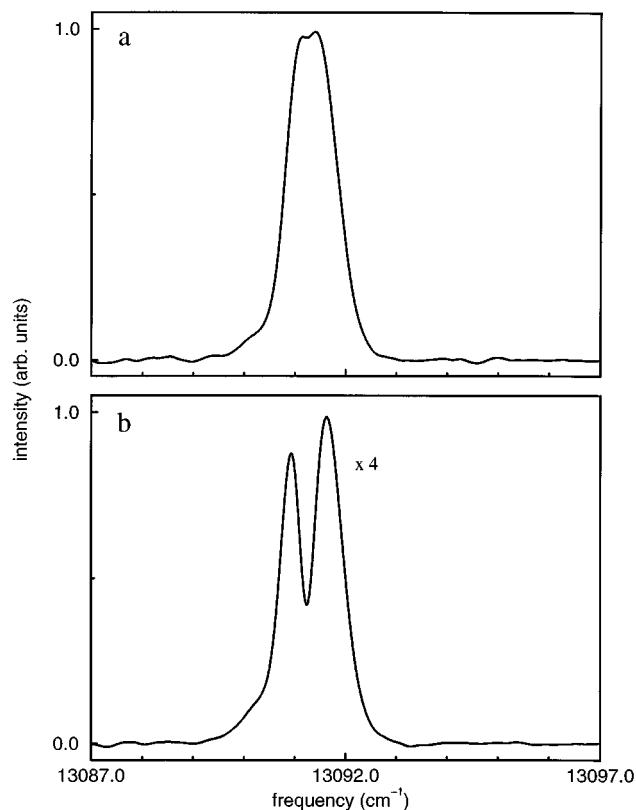


FIG. 3. Fourier transforms of the interferograms presented in Fig. 2. Shown is the spectral intensity distribution at the beginning of the ring-down transient (a) and  $2\ \mu\text{s}$  later (b). Due to absorption by molecular oxygen, the central part of the spectral profile is observed to decay more rapidly than the wings.

and thereby a two-point CRD measurement of the oxygen absorption can be performed.

As pointed out in the previous section, normalized interferograms and intensity calibration with an extra PMT are not needed. To explicitly demonstrate this, a normalized interferogram obtained by dividing the interferogram shown in Fig. 2(b) by the interferogram shown in Fig. 2(a), is shown in Fig. 4. This normalized interferogram does not resemble a

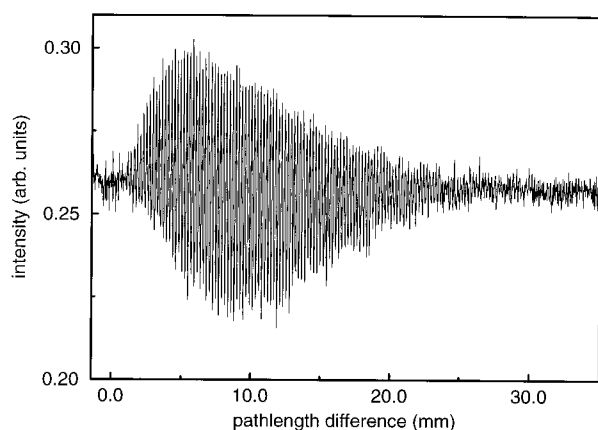


FIG. 4. Normalized interferogram  $I_{\text{norm}}(\Delta, t)$  is obtained by dividing the interferogram shown in Fig. 2(b) by the interferogram shown in Fig. 2(a). This normalized interferogram contains all the required information on the absorption spectrum.

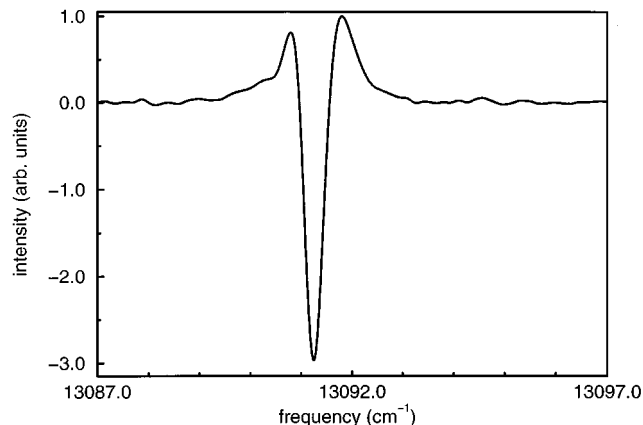


FIG. 5. Fourier transform of the normalized interferogram shown in Fig. 4. This spectrum has to be convoluted with the spectral intensity distribution of the light source to obtain a standard absorption spectrum.

standard interferogram, but contains, nevertheless, all the required absorption information. This is evident from the Fourier transform of the normalized interferogram (shown in Fig. 5). The standard absorption spectrum is recovered from this spectrum after convolution with the spectral intensity distribution of the light entering the cavity.

There are various ways to determine the spectral intensity distribution of the light source, which, for a given experimental setup, has only to be measured once. One way is to measure the intensity corrected interferogram at  $t=0$ , and Fourier transform this to get the spectral intensity distribution. The exact shape of the spectral intensity distribution that is taken is not very critical; when a broadband light source in combination with a bandpass filter is used, as in the experiments discussed below, it is sufficiently accurate to take the spectral intensity distribution to be identical to the spectral transmission function of the filter.

To demonstrate the performance of the FT-CRD spectrometer with a broad-band light source, a  $400\ \text{cm}^{-1}$  wide light pulse is coupled into the ring down cavity. The cavity is filled with 15 mbar of  $\text{O}_2$ . In order to increase the width of the oxygen absorption lines to better match to the spectral resolution of the FT spectrometer 1050 mbar of  $\text{SF}_6$  is added. Still, the intrinsic linewidth of the oxygen lines under these conditions is about a factor three smaller than the  $0.4\ \text{cm}^{-1}$  resolution we could obtain with the FT spectrometer, leading to an apparent reduction in absorption strength. At 3260 discrete mirror positions  $\Delta$  the ring-down transients  $I(\Delta, t)$ , obtained after summing over 200 laser shots, are recorded. With a 50 Hz repetition rate-light source, this implies a total measurement time of almost 4 h. As the actual measurement takes place only during the  $6\ \mu\text{s}$  following the laser pulse, the effective measurement time is less than 4 s. A higher repetition rate light source is, therefore, desirable for these experiments. The data are rearranged and manipulated as described in Sec. III. From the resulting spectra  $I(\nu, t)$ , the frequency dependent ring-down time  $\tau(\nu)$  is deduced. The resulting absorption coefficient  $\kappa(\nu)$ , proportional to  $1/[c\tau(\nu)]$ , is shown as a function of frequency in Fig. 6. The spectral structure observed in this figure is due to the atmospheric band of molecular oxygen, the magnetic dipole al-

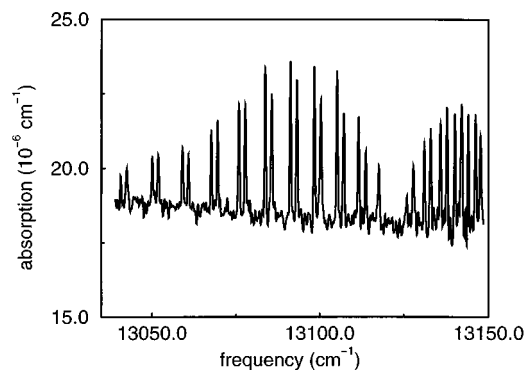


FIG. 6. Absorption spectrum of 15 mbar  $O_2$  in 1050 mbar  $SF_6$  around 763 nm is recorded using pulsed multiplex CRD absorption spectroscopy with the described FT-CRD spectrometer. The spectral structure is due to the atmospheric band, the  $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$  transition, of molecular oxygen.

lowed, spin-forbidden  $b^1\Sigma_g^+, v'=0 \leftarrow X^3\Sigma_g^-, v''=0$  transition.<sup>17</sup>

To the best of our knowledge, in all experiments that have employed time-resolved FT spectroscopy to date, zero background emission processes—like laser induced fluorescence—have been studied. Only a limited number of frequencies are present in the signal in these cases. This is required, because the dynamic range of the fast digitizers that are used to record the time dependent signals is not sufficient to detect minute absorption on a broad continuum of frequencies. Pulse-to-pulse intensity fluctuations are intrinsic to any process induced by a pulsed source make direct time-resolved FT absorption measurements even more difficult.<sup>16</sup>

In the FT-CRD spectrometer presented here, the absorption is deduced from a measurement that is independent of light source intensity fluctuations, and only normalized interferograms are needed. Therefore, less stringent restrictions are imposed on the vertical resolution of the digitizer. The spectrum presented in Fig. 6 is the first direct absorption spectrum recorded using time-resolved FT spectroscopy. From this spectrum, a noise-equivalent absorption detection limit of  $2.5 \cdot 10^{-7} \text{ cm}^{-1}$ , corresponding to an  $1/e$  absorption length of 40 km, is deduced for the present experimental setup. This absorption detection limit even compares favorably to the detection limit that can be obtained using standard continuous FT spectroscopy in a long pathlength absorption cell, although digitizers with a higher dynamic range are then used. If interfaced to pulsed, repetitive sources, many orders of magnitude are gained in absorption detection sensitivity with the FT-CRD technique compared to presently available FT spectroscopic techniques.

The SNR in the spectrum presented in Fig. 6 is still somewhat inferior to the SNR that can be obtained in a CRD experiment using a tunable narrowband laser, under otherwise identical experimental conditions. This can be partly explained by the fluctuations in the spectral intensity distribution of the broad band light source that we have used. In addition, the limitation in the dynamic range of presently available state-of-the-art fast digitizers is more dramatic in the FT experiments than in the experiments where a single frequency light source is used. To be able to use the digitizers with the higher dynamic range in the FT-CRD experi-

ments, the measured transients have to be stored and read out slowly afterward; experiments aiming at this are being undertaken.

## V. CONCLUSIONS

We have experimentally demonstrated that the sensitivity of the CRD absorption detection technique can be combined with the multiplex advantage of FT spectroscopy to form a sensitive pulsed multiplex absorption spectrometer. In FT-CRD spectroscopy, the absorption information is deduced from the temporal shape of the ring down transient; therefore, only the spectral shape of the light source has to be known and has to remain constant during the measurement, whereas the intensity of the light source is allowed to fluctuate. One does not need to know the absolute intensity of the interferograms  $I(\Delta, t)$ , which poses less stringent restrictions to the vertical resolution of the digitizer.

Full advantage of the multiplex approach to spectroscopy is obtained in the (near)-IR spectral region where the intrinsic noise level of the light detectors is higher than in the visible and near-UV range. The Michelson interferometers work better for longer wavelengths. It is anticipated that the FT-CRD technique presented here is ideal for exploration in the spectroscopically valuable IR region of the spectrum.

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