Circular multireflection cell for optical spectroscopy

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Received 20 May 2010; accepted 12 August 2010;
posted 20 August 2010 (Doc. ID 128782); published 9 September 2010

We constructed a circular multireflection (CMR) cell, allowing multireflection around the center of the cell. This is caused by a skewed adjustment of the entering beam (equivalent to a simple parallel shift/offset), avoiding the center of the cell, thus leading to multiple reflections. The experimental setup with a cell with an inner diameter of 6 cm showed up to 17.5 beam passes on polished aluminum and attained path lengths up to 105 cm, demonstrated by Fourier transform infrared measurements of CO_2 gas between 2283 and 2400 cm^{-1}. The circular concept, i.e., the centering of the reflections, is useful for absorption spectroscopy on trace gases and aerosols. The optical alignment of the cell can completely be performed from outside the experimental setup, e.g., an aerosol flow reactor or a vacuum system. The variation of the path length is easily possible by adjusting the position of the cell with respect to the entering light beam.

OCIS codes: 080.4035, 120.5700, 300.0300.

1. Introduction

Based on the concepts of White [1] and Herriott *et al.* [2], various types of multireflection optical devices have been designed. A recent overview of those cells has been published by Robert [3]. All these cells are characterized by reflecting the beams along a special axis of the optical setup. The beamlines of those setups are not focused on a special point. Hence, a complete and homogeneous filling of the space within the measuring cell is needed to utilize the overall optical path. Recent developments of cavity-enhanced spectroscopy are limited to a small spectral range [4]. Recording spectra in the entire middle infrared range is still not possible.

To study the formation process or the processing of secondary organic aerosols using infrared spectroscopy, aerosol flow reactors are very useful because of their high temporal resolution [5]. The organic precursor or aerosol stream, located in the center of the gas flow, is encircled by a reactant gas or shielding air stream in order to diminish deposition of particles. To couple an aerosol flow reactor to a long-path optical device for infrared spectroscopy with higher detection limits, White-cell optics have been used [6]. Those very small White cells come up with some disadvantages: apart from the difficulty to adjust those devices inside the experimental setup or the vacuum system, only a small fraction of the overall beam is passing the precursor or aerosol stream centered inside the cell, which is the section of utmost interest.

Hence a circular multireflection (CMR) cell, which focuses the infrared beam through or next to the center of the cell, appears to be more appropriate. Such a multireflection cell was constructed using single mirrors and allowing an increase of the path length by a factor of 8 [7]. However, the path length cannot be varied, and there is still the need of adjusting every single mirror inside the experimental setup.

2. Design of Circular Multireflection Cell

A. Geometric Concept

The basic geometric concept of the CMR cell is shown in Fig. 1. The cell is equipped with two apertures for the beam to enter and to leave at positions A and E, defining the angle ε. The entering beam at A is reflected at position B. The angle of reflection β is dependent on the offset d of the two apertures from the

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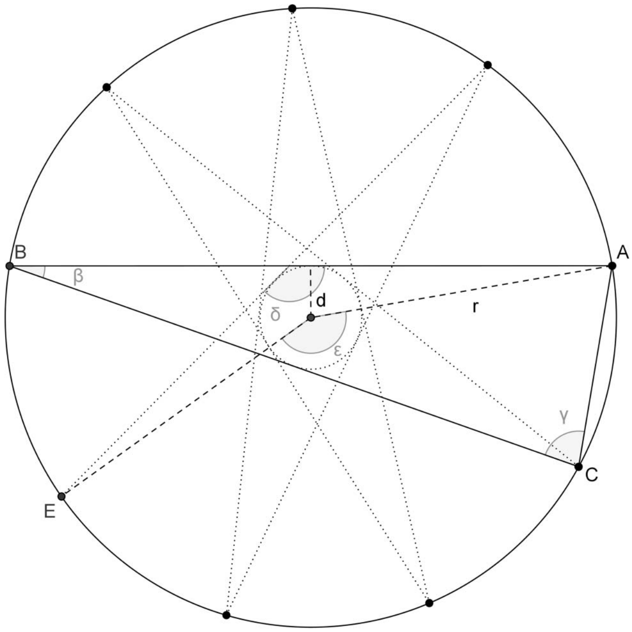

Fig. 1. Geometric concept of CMR cell: A, entrance of the beam into the cell; B, point of first reflection; E, exit of the beam; d, offset of the beam; r, mirror radius of the CMR cell; β, angle of reflection; δ, angle between the offsets of the entering and leaving beams; and ε, angle between entrance A and exit E. The distance AC, which is limited by the size of the aperture at position A, limits the achievable number of reflections.

center of the cell. After multiple reflections inside the cell, the beam leaves the cell at position E. Thus, only angles of reflection β and therefore beam offsets d are permitted, which allow the beam to exit the cell at position E. This limitation is described by Eq. (1) and the factor n. The number of reflections R is $2n - 1$:

$$2n\beta = \varepsilon \quad \text{with} \quad n \in N. \tag{1}$$

Hence, the offset of the beam (2) and the angle of reflection (3) are functions of the limiting factor n, the offset d and the radius r of the cell:

$$d = r \sin \frac{\varepsilon}{4n}, \tag{2}$$

$$\beta = 2 \arcsin \frac{d}{r}. \tag{3}$$

The angle δ between entrance and exit beam is given by Eq. (4):

$$\delta = \varepsilon - \beta. \tag{4}$$

To calculate the length of the optical path, the length of line A to B was calculated according to Eq. (5). The total path length is given in Eq. (6):

$$\overline{\mathrm{AB}} = 2r \sin \frac{180 - \beta}{2}, \tag{5}$$

$$L = 2n\overline{\mathrm{AB}}. \tag{6}$$

A further limitation is the size of the apertures at A and E. If line AC (7) is below the diameter of the apertures, parts of the entering beams are lost by transmission out of the cell:

$$\overline{\mathrm{AC}} = 2r \sin \beta. \tag{7}$$

B. Design

The CMR cell is an aluminum cylinder with an outer diameter of 80 mm and a height of 30 mm with a polished spherical reflecting surface inside, focusing the light beam to the opposite walls. The radius r of this concave mirror is 30 mm. The angle ε, which determines the position of the two apertures, was set to 165° because of the optical bench that was used to adjust the beams. The infrared light beam was adjusted to have its focus at the center of the cell. The offset d of the beams was set to 5 mm, leading to an angle δ of the beams of 145.8°. Because of the optical bench and the width of the infrared beam, the diameter of the apertures was set to 12 mm. Hence, offsets between 0 and 11 mm are possible when the overall beam does not need to be transmitted through the cell. The design of the cell is shown in Fig. 2. The cell was machined on a computed numerically controlled (CNC) lathe from an aluminum cylinder. The possible path lengths and related offsets are shown in Fig. 3. More than four reflections ($n = 2$) are needed because of the maximum offset of 11 mm. The length of the segment AC is limited to 12 mm because of the diameter of the entrance aperture. Hence, a maximum of 14 reflections ($n = 7$) is possible without losing parts of the reflected beam,

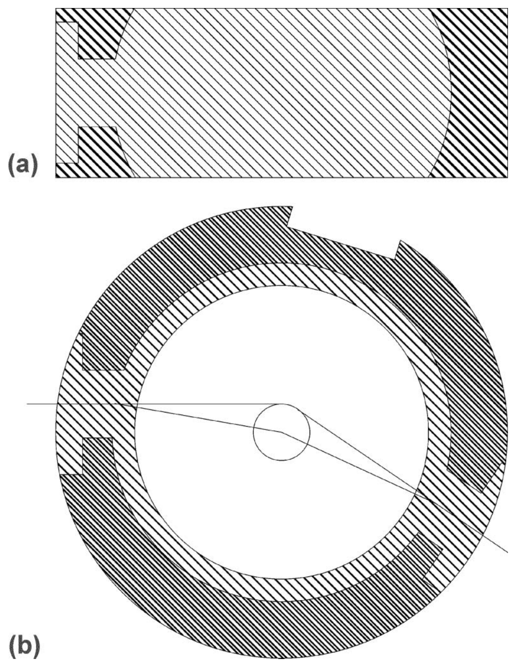

Fig. 2. Design of CMR cell: (a) view from side showing cell design with aperture and (b) view from top with entrance and exit apertures at angle of $\varepsilon = 165°$ and offset of 5 mm.

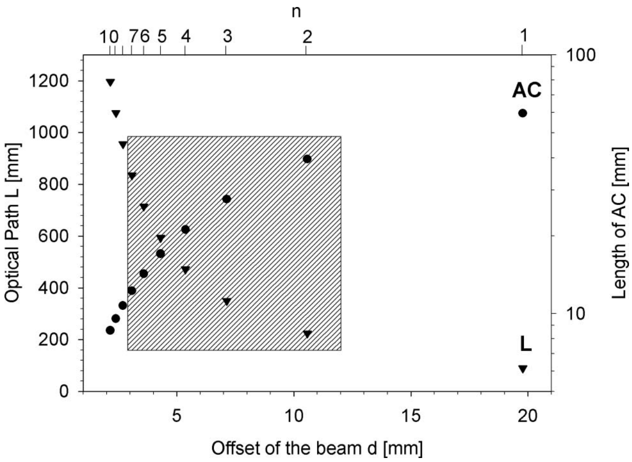

Fig. 3. Path lengths calculated for the designed cell (Fig. 2)—this cell can be operated at offsets up to 12 mm and lengths of line AC down to 12 mm (both limited by the width of the apertures).

leaving the cell through the entrance aperture. These limitations lead to path lengths between 230 and 840 mm. Accepting the beam to be only half reflected—the other part is lost by the entrance aperture—path lengths up to 1800 mm (30 reflections) are possible. The volume of the CMR cell was calculated to be 78 cm^3.

C. Experimental Setup

The CMR cell was mounted on an optical bench for Bruker FTIR spectrometers (Fig. 4). The cell could be adjusted vertically and at a right angle to the entire optical path of the spectrometer. The infrared beam is deflected by a mirror on a focusing gold-coated mirror, which reflects the beam into the center of the cell. The focal point of the focusing mirror is adjusted close to the center of the cell. The multireflected beam leaving the cell is collected by a second gold-coated focusing mirror and reflected to a fourth mirror, which couples the beam into the optical path of the spectrometer.

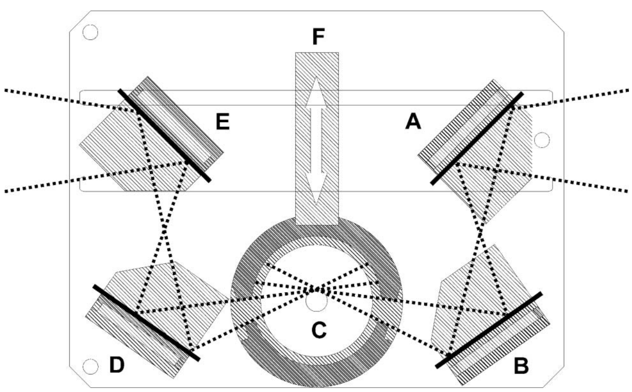

Fig. 4. Circular multireflection cell mounted on an optical bench for Bruker FTIR spectrometers: the infrared beam is focused using mirrors A and B into the CMR cell C. Mirrors D and E focus the beam back into the spectrometer. The position of the cell, and hence the optical path length, can be varied by moving the translation stage F.

For characterization of the CMR cell with gaseous samples, the two apertures were equipped with windows. Plane-parallel KBr windows with a diameter of 20 mm and a height of 4 mm were used. The top and the bottom were closed using stainless steel plates, equipped with connectors to flush the cell with the gaseous sample.

The characterization of the CMR cell was performed using a Bruker 113v FTIR spectrometer with a compartment for optical devices that operate at normal pressure. This infrared spectrometer is supplied with dry, almost CO_2-free air (Balston, 75–60) and evacuated down to 60 mbar to diminish distortion of the spectra by CO_2, water, methane, and other remaining background traces. All spectra were taken at a spectral resolution of 0.1 cm^{-1} using a mercury cadmium telluride detector, and 128 single-sided interferograms were co-added each before Fourier transformation. Post processing and baseline correction of the infrared spectra were performed using the Bruker software package OPUS, version 5.0.

3. Characterization of Circular Multireflection Cell

The length of the optical path of the CMR cell was characterized using a mixture of 300 ppm CO_2 in purified air (Fig. 5). The concentration of ozone was controlled using an LI-COR LI-820 CO_2 analyzer. The optical path of the CMR cell was adjusted to a parallel offset of 5 mm. Offsets above 5 mm were neglected because they do not fit the geometric concept. The offset was decreased to 0 mm in steps of 0.5 mm by moving translation stage F (Fig. 4), and the absorptions at different offsets of the beam were integrated between 2400 and 2283 cm^{-1}. The absorption at 0 reflections was measured using a 6 cm absorption cell, which equals the base length of the CMR cell. Integration was performed after baseline correction using the OPUS 5.0 software package. Reflections and path lengths were calculated using the ratio of long-path absorption to the absorption at 0 reflections. The beam throughput represents the attenuation of the infrared beam caused by the decrease of the offset of the optical path.

The path lengths achieved differ from the calculated path lengths caused by the width of the infrared

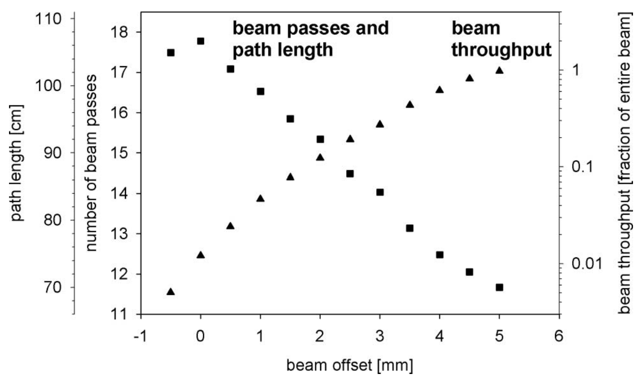

Fig. 5. Measured optical path lengths and beam passes as a function of the offset of the beam. The overall beam throughput of the CMR cell is decreased by a magnitude of 100.

beam in comparison with the theoretical calculation of the path described above. As shown in Fig. 5, using an adjusted offset of 0 mm, a path length of 105 cm could be achieved, which equals about 17.5 theoretical beam passes.

4. Conclusions

The concept of a CMR cell allows multireflection, depending on the cell diameter and the offset of the entering beam. Using the described setup, path lengths up to 105 cm could be achieved. Based on the diameter of the cell of 6 cm, the absorption of the sample gas could be enhanced 17.5 times. Therefore, at least 17.5 beam passes must have been achieved at a theoretical reflectance of the cell material of 100%. The alignment of the CMR cell is completely possible outside the cell. Hence, vacuum systems or cramped experimental setups do not need to be opened to adjust the beam inside the cell. Further, the length of the optical path can easily be varied by sliding the cell relative to the entering beam. Multireflecting the infrared beam around the center of the cell optimized the CMR cell for flow systems that use shield air and the product gas or particle stream inside the shield. Further optimization such as focus and width of the beam and lowering the diameter of the entrance and exit apertures will increase the number of reflections and decrease the loss of the beam. Also, the position of the two apertures related to the parallel offset could be optimized.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the research unit HALOPROC and by the European Union (EU) within the infrastructure EUROCHAMP.

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