

Spectroscopic study of the ν_1 band of SO_2 using a continuous-wave DFB QCL at $9.1 \mu\text{m}$

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ABSTRACT We report results of spectroscopic measurements with a continuous-wave distributed-feedback quantum-cascade laser (DFB QCL). Line intensities and self-broadening coefficients were measured in the ν_1 band of SO_2 between 1088 and 1090 cm^{-1} . The self-broadening coefficients in this paper confirm the typical decrease of γ_{self} with increasing rotational quantum number K_a'' . The line intensities determined here are smaller than those in the HITRAN 2000 database. Several lines found in this study were not present in the database.

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1 Introduction

Since the first realization of a QCL [1] in 1994, many applications have been studied: communications [2] (for example, high-speed digital data transmission [3] and optical free-space high-speed links [4]), detection and quantification of trace gases, and high-resolution spectroscopy. For example, the detection of gases such as NO , CO , CO_2 , and NH_3 , which play an important role in monitoring biomedical function, has been carried out [5,6]. QCL's have also been used to detect methane and nitrous oxide isotopomers near $8.1 \mu\text{m}$ [7]. Spectroscopic detection sensitivities of trace gases down to the one part in 10^9 (ppb) concentration level have been obtained using a $7.9\text{-}\mu\text{m}$ QCL, a 100-m -path-length multipass cell, and a zero-air background subtraction technique. Detection of CH_4 , N_2O , H_2O , and $\text{C}_2\text{H}_5\text{OH}$ in ambient air has been achieved [8].

We report here spectroscopic studies of the ν_1 band of SO_2 using a QCL from Alpes Lasers (Switzerland). Line intensities and self-broadening coefficients were measured. The results are compared with previous determinations and theoretical predictions.

Sulfur dioxide is an atmospheric relevant molecule of the C_{2v} symmetry group. SO_2 is a very important molecule because of its ubiquitous presence in our polluted atmosphere. It is one of the primary pollutants in acid rain. The ν_1 band of SO_2 is centered at 1151 cm^{-1} . Line positions and intensi-

ties have been reported by Guelachvili et al. [9] and Flaud et al. [10].

Line-broadening coefficients have been investigated by Tejwani [11], who applied the Anderson–Tsao–Curnutte theory. In his calculations Tejwani predicted pronounced differences between the rotational quantum number dependencies of A-type (ν_3 , $\nu_1 + \nu_3$) and B-type (ν_1 , ν_2) bands. The line intensities and self-broadening coefficients were precisely investigated in the ν_1 band by Sumpf [12, 13] with a pulse-driven diode laser spectrometer and by Chu [14] by Fourier transform spectroscopy, in the ν_2 band by Sumpf [15], in the ν_3 band by Kühnemann [16] and Sumpf [13, 17], and in the $\nu_1 + \nu_3$ band [18, 19] using a pulse lead-salt diode laser spectrometer. The variation of the broadening coefficients and rotational quantum numbers predicted by Tejwani for B-type bands was observed (decrease of the self-broadening coefficient with increasing K_a''), but without a vibrational dependence.

2 Experimental details

The SO_2 spectra were recorded at high resolution in the laboratory with a QCL. Our experimental arrangement is schematically shown in Fig. 1. The QCL is housed inside a laboratory-built cryostat filled with liquid nitrogen. The QC laser works from 80 to 130 K and the threshold current is 445 mA . The temperature is controlled and stabilized by a model Lakeshore 340. Its long-term (several second) temperature stability is $\pm 0.02 \text{ K}$, but its short-term stability (less than 1 s) is better. The current source is an ILX lightwave model LDC 3744B. The current stability is about $50 \mu\text{A}$ and the set-point accuracy is 0.05% . The QCL beam was collected by a parabolic mirror and was separated into two parts via a ZnSe beam splitter (BS). The reflected beam (channel A) was coupled with a spherical Fabry–Perot etalon (SFP) used for relative frequency calibration (with a free spectral range of 0.01 cm^{-1}). The second beam (channel B) was passed through a 19.76-cm -long gas cell filled with SO_2 (provided by UCAR, purity $\geq 99.98\%$). Both beams were focused by parabolic mirrors on two HgCdTe photodetectors. The data acquisition was made with a lock-in technique. We used a computer to collect all data. Wavenumber sweeping was obtained by applying a temperature ramp to the QCL. Using this technique, we

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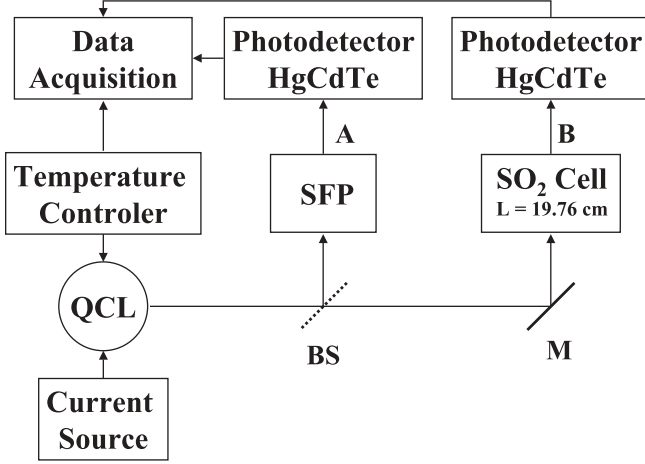


FIGURE 1 Experimental arrangement. QCL stands for quantum cascade laser, SFP for spherical Fabry-Perot (free spectral range = 0.01 cm^{-1}), BS for beam splitter, and M for mirror

scanned more SO_2 lines on the same spectra than with current tuning [20]. A spectrum was recorded with a continuous temperature ramp from 85 to 120 K for about 2 min. The tunability range of the QCL is 1088.0 cm^{-1} at $T = 120 \text{ K}$ and $I = 750 \text{ mA}$ to 1090.65 cm^{-1} at $T = 87.4 \text{ K}$ and $I = 600 \text{ mA}$. The temperature tuning rate is between $-6.62 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ for $I = 600 \text{ mA}$ and $-7.01 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ for $I = 800 \text{ mA}$ and the current tuning rate is about $-2.59 \text{ cm}^{-1} \text{ A}^{-1}$. We obtained several spectra at various pressures (around 1, 5, and 10 Torr) and various currents (0.6, 0.65, and 0.75 A). Table 1 summarizes the experimental conditions of our measurements. The SO_2 pressure was measured with an uncertainty of 0.5% using a MKS baratron manometer with a full scale of 10 Torr. Figure 2a shows a spectrum with a SO_2

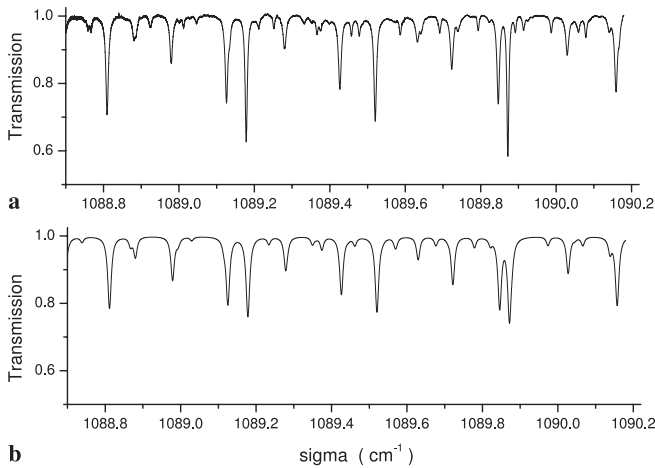


FIGURE 2 Example of recorded spectrum (a) and calculated spectrum (b) with HITRAN 2000 under the same experimental conditions ($P = 9.98 \text{ Torr}$, $T = 289 \text{ K}$, $l = 19.76 \text{ cm}$)

	$I = 600 \text{ mA}$	$I = 650 \text{ mA}$	$I = 750 \text{ mA}$						
Pressure (Torr)	1.22	5.39	9.89	1.05	5.52	9.98	1.01	5.55	10.07

TABLE 1 Gas pressure and laser current for all recorded spectra

pressure of 9.98 Torr, a gas temperature of $T = 289 \text{ K}$, and a QCL current of $I = 650 \text{ mA}$. Figure 2b is the calculated spectrum using the HITRAN 2000 database [21] for the same experimental conditions. We observed discrepancies in the line intensities and linewidths. Some lines are not in the database.

3 Data inversion

We want to determine the self-broadening coefficient γ_{self} and intensity S_0 of SO_2 at 296 K to compare our measurements with HITRAN 2000. To retrieve the absolute intensity and self-broadening coefficient of a line, we fitted a Voigt profile to the molecular transmission. The molecular transmission $T(\sigma)$ was obtained from the SFP (signal A) and SO_2 cell (signal B) signals in two steps. First, the SFP signal was used to retrieve the frequency variation law by a third-degree polynomial interpolation of the interference fringes. In the second step, we retrieved the molecular transmission $T(\sigma)$ from the direct absorption signal A by using

$$A = A_0 T(\sigma). \quad (1)$$

A_0 is what would be the laser flux in the absence of an absorber in the cell. A_0 was obtained from signal A by a third-degree polynomial interpolation over the full transmission region. The line intensity $S(T)$ is related to the molecular transmission through the Beer-Lambert law:

$$T(\sigma) = \frac{I_r(\sigma)}{I_0(\sigma)} = \exp[-k(\sigma, T, P) n l]. \quad (2)$$

n is the density of absorbing molecules along the optical path of length l . The absorption coefficient $k(\sigma, T, P)$ at a temperature T and for a gas pressure P was modeled using the Voigt profile.

The Voigt profile may be expressed as the real part of the complex probability function, which can be evaluated using the Humlicek algorithm [22]. The line intensity at the temperature T is related to the intensity S_0 at the reference temperature $T_0 = 296 \text{ K}$ by

$$S(T) = S_0 \frac{Q_v(T_0)}{Q_v(T)} \frac{Q_r(T_0)}{Q_r(T)} \exp \left\{ -\frac{hcE_0}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\}, \quad (3)$$

where E_0 is the energy of the lower level expressed in cm^{-1} and Q_v and Q_r are, respectively, the vibrational and rotational partition functions. $\frac{Q_r(T_0)}{Q_r(T)}$ was expressed as $\left(\frac{T_0}{T}\right)^{1.5}$ and the influence of the vibrational partition function was neglected, reducing (3) to

$$S(T) = S_0 \left(\frac{T_0}{T}\right)^{1.5} \exp \left\{ -\frac{hcE_0}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\}. \quad (4)$$

The linewidth of our QCL was measured by heterodyning with a $^{12}\text{C}^{18}\text{O}_2$ laser. In this experiment the free-running QCL beam was mixed with a waveguide isotopic $^{12}\text{C}^{18}\text{O}_2$ laser onto a high-speed HgCdTe photomixer and beat notes were recorded from a radio-frequency spectral analyser. The linewidth of our QCL is between 1 and 6 MHz [23]. We verified that there was no additional spectral broadening due

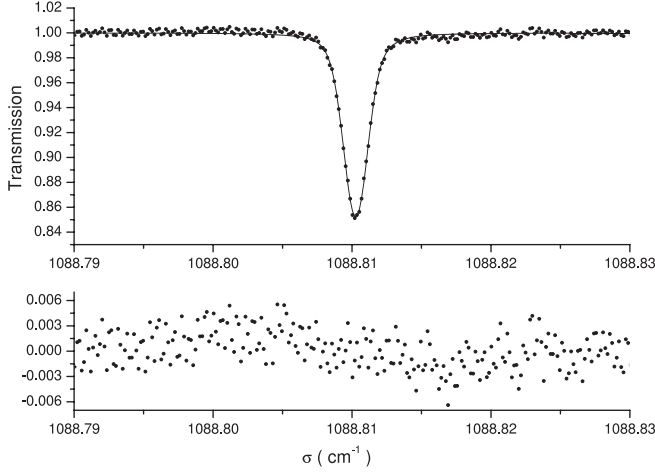


FIGURE 3 Example of recorded spectrum at $1088.8143 \text{ cm}^{-1}$ (laser current = 600 mA SO_2 pressure = 1.22 Torr, $T = 289 \text{ K}$, $l = 19.76 \text{ cm}$) with fitted Voigt profile on the *upper* part and the residual on the *lower* part

to the ramp. Thus the apparatus function of our spectrometer is negligible. One example of a recorded spectrum at $1088.8143 \text{ cm}^{-1}$ is presented in Fig. 3 with a fitted Voigt profile and the residual.

4 Results

The laser allows the range between 1088 and 1090 cm^{-1} to be studied. The intensity S_0 and self-broadening coefficient γ_{self} of nine transitions belonging to the ν_1 vibrational band are reported here. Many other lines were studied during this work and were taken into account in the data inversion but are not reported. The main reasons are that those lines were either too close to a stronger line or too weak to allow accurate measurement. For each line, several spectra were available, corresponding to different currents and temperatures of the QCL. For each spectrum, an individual baseline was calculated and used to obtain the molecular absorption (1). The intensity $S(T)$ and broadening parameter were obtained for a gas temperature of $T = 289 \pm 1 \text{ K}$.

The intensity S_0 at 296 K was then calculated by using (4). For each line, the averaged values of S_0 and γ_{self} are presented in Table 2 and are compared with the HITRAN 2000 database.

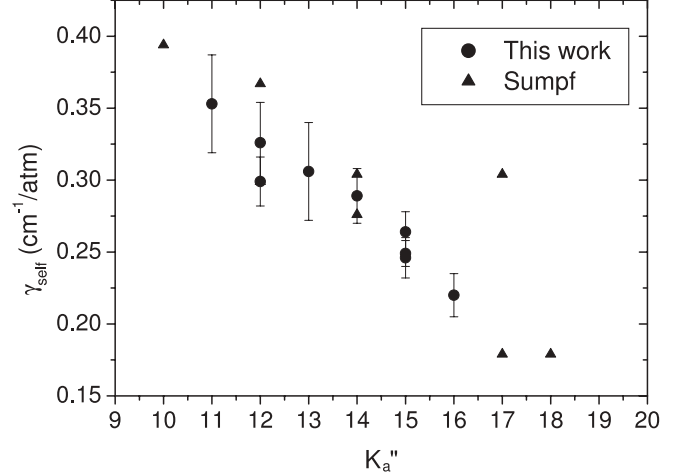


FIGURE 4 Dependence of the self-broadening coefficient γ_{self} on the rotational quantum number K_a''

For each of the studied lines, Table 2 gives the wavenumber, the rotational quantum number, the intensity and broadening coefficient from the HITRAN database, the measured S_0 and γ_{self} , and the ratio $S_{\text{exp}}/S_{\text{HITRAN 2000}}$. For each line, the reported error corresponds to one standard deviation, obtained by averaging the different measurements. This statistical error allows all effects to be taken into account. All our results are smaller than those of HITRAN.

The average ratio $S_{\text{exp}}/S_{\text{HITRAN 2000}}$ in the ν_1 band is equal to (0.82 ± 0.02) and is comparable with the value from [13]: (0.83 ± 0.02) .

In Fig. 4, the self-broadening coefficient is plotted versus the rotational quantum number K_a'' . We observed a decrease of γ_{self} with an increase of K_a'' . Data measured with a lead-salt diode laser spectrometer in the ν_1 band [13] are also plotted. Our results agree with this work. The same evolution of γ_{self} with K_a'' has been seen in the ν_1 band [12, 13], ν_2 band [15], ν_3 band [13, 16, 17], and $\nu_1 + \nu_3$ band [18, 19]. We did not have enough measurements to make a conclusion about the variation of γ_{self} with J'' . We have shown that the QCL is efficient for high-resolution spectroscopy. A lot of weak lines were observed that are not in the HITRAN database. As an example, Fig. 5 presents the experimental spectrum between 1089.39

$\sigma \text{ (cm}^{-1}\text{)}$	HITRAN2000						$S_{\text{HITRAN 2000}}$ ($10^{-22} \text{ cm}^{-1}/\text{molecule cm}^{-2}$)	γ_{self} ($\text{cm}^{-1}/\text{atm}$)	Our Measurements		
	J'	$K'a$	$K'c$	J''	$K''a$	$K''c$			S_{exp} ($10^{-22} \text{ cm}^{-1}/\text{molecule cm}^{-2}$)	γ_{self} ($\text{cm}^{-1}/\text{atm}$)	$S_{\text{exp}}/S_{\text{HITRAN 2000}}$
1088.0993	22	14	8	23	15	9	5.80	0.39	4.76 ± 0.15	0.246 ± 0.014	0.82 ± 0.03
1088.4015	26	13	13	27	14	14	5.27	0.39	4.43 ± 0.16	0.289 ± 0.019	0.84 ± 0.03
1088.8114	21	14	8	22	15	7	6.18	0.39	5.12 ± 0.17	0.249 ± 0.009	0.83 ± 0.03
1088.9780	34	11	23	35	12	24	3.64	0.39	2.91 ± 0.22	0.326 ± 0.028	0.80 ± 0.06
1089.1782	16	15	1	17	16	2	6.78	0.39	5.87 ± 0.14	0.220 ± 0.015	0.87 ± 0.02
1089.2786	38	10	28	39	11	29	2.74	0.39	2.13 ± 0.12	0.353 ± 0.034	0.78 ± 0.04
1089.4261	29	12	18	30	13	17	4.92	0.39	4.16 ± 0.25	0.306 ± 0.034	0.85 ± 0.05
1089.5204	20	14	6	21	15	7	6.57	0.39	5.67 ± 0.21	0.264 ± 0.014	0.86 ± 0.03
1089.7216	33	11	23	34	12	22	4.01	0.39	2.99 ± 0.18	0.299 ± 0.017	0.75 ± 0.05

TABLE 2 Compilation of the measured self-broadening coefficients and line intensities in the ν_1 band of SO_2 . Line positions are from the HITRAN 2000 database. For each line the reported error corresponds to one standard deviation, obtained by averaging the various measurements

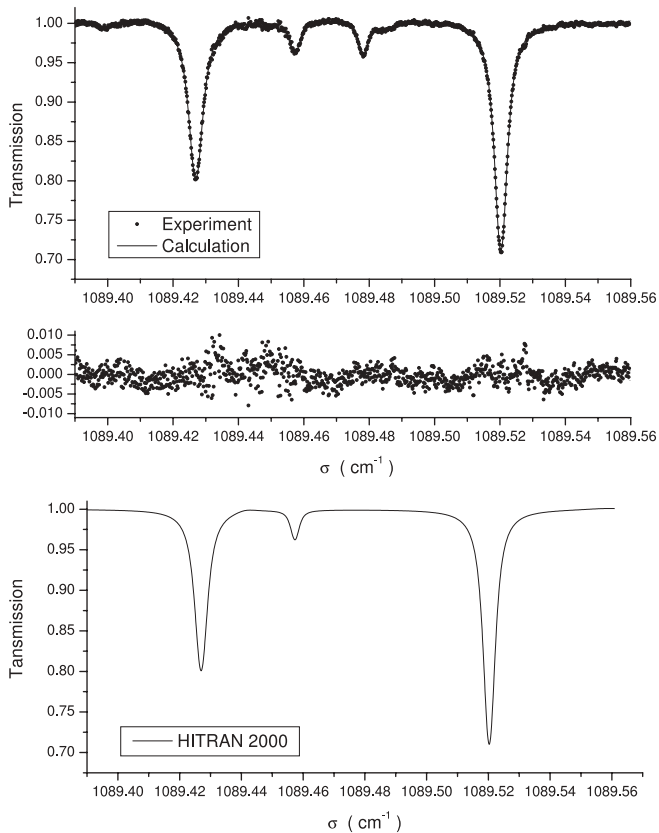


FIGURE 5 *Top*: the experimental and fitted profiles, between 1089.39 and 1089.56 cm^{-1} . *Middle*: the residual for the above spectrum. *Bottom*: the spectrum between 1089.39 and 1089.56 cm^{-1} obtained using HITRAN parameters under the same experimental conditions ($P = 9.98$ Torr, $T = 289$ K, $l = 19.76$ cm)

to 1089.56 cm^{-1} and the calculated spectrum using HITRAN 2000. This figure shows the presence of numerous weak lines. As the purity of the gas was $\geq 99.98\%$, these lines do not originate from other species. They may be hot band transitions, other isotopomers, or weaker transitions not included in the HITRAN 2000 database.

5 Conclusion

This paper shows high-resolution spectrometry with a cw QCL. Line intensities and self-broadening coefficients in the ν_1 band of SO_2 around 9.1 μm were studied experimentally with a continuous-wave DFB QCL. We found

the same evolution of γ_{self} with K_a'' as Sumpf. The measured line intensities in the ν_1 band were on average (0.82 ± 0.02) times those reported in the HITRAN 2000 database. This article is evidence that the QCL will be used more widely for spectroscopy in the future.

REFERENCES

- 1 J. Faist, F. Capasso, D.L. Sivco, C. Sirtori, A.L. Hutchinson, A.Y. Cho: *Science* **284**, 553 (1994)
- 2 F. Capasso, R. Paiella, R. Martini, R. Colombelli, C. Gmachl, T.L. Meyers, M.S. Taubman, R.M. Williams, C.G. Bethea, K. Unterrainer, H.Y. Hwang, D.L. Sivco, A.Y. Cho, A.M. Sergent, H.C. Liu, A. Whittaker: *IEEE J. Quantum Electron.* **QE-38**, 511 (2002)
- 3 R. Martini, R. Paiella, C. Gmachl, F. Capasso, E.A. Whittaker, H.C. Liu, H.Y. Hwang, D.L. Sivco, J.N. Baillargeon, A.Y. Cho: *Electron. Lett.* **37**, 21 (2001)
- 4 R. Martini, C. Bethea, F. Capasso, R. Paiella, E.A. Whittaker, H.Y. Hwang, D.L. Sivco, J.N. Baillargeon, A.Y. Cho: *Electron. Lett.* **38**, 4 (2002)
- 5 L. Menzel, A.A. Kosterev, R.F. Curl, F.K. Tittel, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, A.Y. Cho, W. Urban: *Appl. Phys. B* **72**, 859 (2001)
- 6 A.A. Kosterev, F.K. Tittel, W. Durante, M. Allen, R. Köhler, C. Gmachl, F. Capasso, D.L. Sivco, A.Y. Cho: *Appl. Phys. B* **74**, 95 (2002)
- 7 G. Gagliardi, F. Tamassia, P. De Natale, C. Gmachl, F. Capasso: *Eur. Phys. J. D* **19**, 327 (2002)
- 8 A.A. Kosterev, R.F. Curl, F.K. Tittel, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, A.Y. Cho: *Appl. Opt.* **39**, 4425 (2000)
- 9 G. Guelachvili, O.V. Naumenko, O.N. Ulenikov: *J. Mol. Spectrosc.* **125**, 128 (1987)
- 10 J.M. Flaud, A. Perrin, L.M. Salah, W.J. Lafferty, G. Guelachvili: *J. Mol. Spectrosc.* **160**, 272 (1993)
- 11 G.D.T. Tejwani: *J. Chem. Phys.* **57**, 4676 (1972)
- 12 B. Sumpf, O. Fleischmann, H.D. Kronfeldt: *J. Mol. Spectrosc.* **176**, 127 (1996)
- 13 B. Sumpf: *J. Mol. Struct.* **599**, 39 (2001)
- 14 P.M. Chu, S.J. Wetzel, W.J. Lafferty, A. Perrin, J.-M. Flaud, P. Arcas, G. Guelachvili: *J. Mol. Spectrosc.* **189**, 55 (1998)
- 15 B. Sumpf: *Spectrochim. Acta, Part A* **55**, 1931 (1999)
- 16 F. Kühnemann, Y. Heiner, B. Sumpf, K. Herrmann: *J. Mol. Spectrosc.* **152**, 1 (1992)
- 17 B. Sumpf, M. Schöne, H.D. Kronfeldt: *J. Mol. Spectrosc.* **179**, 137 (1996)
- 18 B. Sumpf: *J. Mol. Spectrosc.* **181**, 160 (1997)
- 19 B. Sumpf: *J. Mol. Spectrosc.* **186**, 249 (1997)
- 20 D. Weidmann, D. Courtois: *Infrared Phys. Technol.* **41**, 361 (2000)
- 21 L.S. Rothman, R.R. Gamache, A. Goldman, L.R. Brown, R.A. Toth, H.M. Pickett, R.L. Poynter, J.M. Flaud, C. Camy-Perey, A. Barbe, N. Husson, C.P. Rinsland, M.A. Smith: *Appl. Opt.* **26**, 4058 (1997)
- 22 J. Humlicek: *J. Quant. Spectrosc. Radiat. Transfer* **27**, 437 (1982)
- 23 D. Weidmann, L. Joly, V. Parpillon, D. Courtois, Y. Bonetti, T. Aellen, M. Beck, J. Faist, D. Hofstetter: *Opt. Lett.* **28**, 704 (2003)