

Research Article

Fourier Transform and Photoacoustic Absorption Spectra of Ethylene within 6035–6210 cm^{-1} : Comparative Measurements

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Measurements of ethylene absorption spectra with Fourier Transform (FT) and Photoacoustic (PA) spectrometers within 6035–6210 cm^{-1} are described. The methodology used for building the frequency scale for both spectrometers is presented. The methane absorption spectrum, included into the HITRAN database, was used in both cases to calibrate the frequency scale. Ethylene absorption spectra were obtained with the two recording methods; a coincidence of the measured line center positions was obtained with an accuracy of 0.0005 cm^{-1} .

1. Introduction

The ethylene is a natural component of the atmospheric air, which actively participates to various chemical processes. As it is also a hormone for the growth of plants, its influence on the plant biochemistry, ecology, and metabolism of human beings and animals is of significant interest for several areas of research. Because of its very high activity relative with hydroxyl (OH), ethylene affects the ozone concentration in the atmosphere. All these factors make it an important contaminant, therefore, the monitoring of its atmospheric concentration, sources, and sinks is of great investigation importance.

The background content of the ethylene in the atmosphere is within 10–50 ppb. The global ethylene emission into the atmosphere is roughly estimated as 18–45 millions of tons per year; among them 74% are due to natural sources, and 26% are due to anthropogenic ones; the major ethylene sink is determined by reactions with the radical OH (85%) and ozone (15%) [1].

Infrared radiation (IR) laser spectroscopy due to its high sensitivity and resolution is a valid multicomponent detection method, complementary to other well-proven techniques like, for example, mass spectrometry and gas chromatography. The use of continuously tunable diode

lasers coupled with high sensitive techniques, like Photoacoustic and cavity ring down spectroscopy, started to be wide application few years ago, when cheap and reliable lasers diodes started to be available in the range of 1.5–1.8 μm , where a lot of interesting molecules like H_2O , CO_2 , CH_4 , CO , and C_2H_4 present absorption combination and overtone bands. The monitoring of the concentration of these molecules necessitates high accurate information about their absorption spectra: line-center positions, intensities, spectral line shape contours, broadening coefficients, and line-center shifts. Absorption spectra of H_2O , CO_2 , CH_4 , and CO in 1.65 μm region are available in the present-day databases with however some incompleteness (data relative to pressure line-center shifts are absent) and errors (in particular on line-center positions, intensities, and air coefficient broadenings).

The C_2H_4 spectrum available in databases is limited to few spectral range around 1000 and 3000 cm^{-1} . As a rule the literature data on the ethylene absorption spectrum are only reported in reviews, which do not allow its retrieval with a satisfactory accuracy. In the 5900–6400 cm^{-1} range [2] the ethylene absorption spectrum is recorded at a low resolution (5 cm^{-1}). The ethylene Fourier Transform (FT) spectrum at a resolution of 0.02 cm^{-1} in a supersonic flow is reported in [3] and at a resolution of 0.015 cm^{-1} in the 6070–6230 cm^{-1} range

in [4], as well as opto-acoustic and opto-thermal spectra in the 6147–6170 cm^{-1} range in a collimated beam. The error in the determination of line-centers in [4] is equal to 0.004 cm^{-1} . The C_2H_4 spectrum with a high resolution in individual spectral fragments was reported in [5] (6154–6159 cm^{-1}), [6] (6149.7–6150.48 cm^{-1}), and [7] (6157.55–6158.25 cm^{-1}). Earlier, the authors of [8] presented the ethylene absorption spectrum in the 6035–6210 cm^{-1} range, recorded with the use of a two-channel PA spectrometer combined with the diode laser, characterized by a threshold absorption sensitivity of $1.4 \cdot 10^{-6} \text{ cm}^{-1}$. The comparison of the ethylene absorption spectrum [8] with data presented in [4–7] has shown a discrepancy in line-center positions from 0.005 cm^{-1} [6] to 0.32 cm^{-1} [7]. The ethylene absorption cross-sections were reported only in [6].

To verify the data presented in [8] the ethylene absorption spectrum in the 6035–6210 cm^{-1} range was recorded with the use of a high resolution FT spectrometer Bruker IFS 125HR (France, Institute Carnot de Bourgogne) [9]. The systematic inaccuracy in line-center positions determination ($\sim 0.025 \text{ cm}^{-1}$) for these two data was observed.

In this work, the ethylene absorption spectrum was recorded in the 6030–6250 cm^{-1} range with the use of a high resolution FT spectrometer Bruker IFS 125HR (Russia, Tomsk, IAO SB RAS) and two-channel Photoacoustic spectrometer with a diode laser (DOAS DL). The methane absorption spectrum [10, 11] was used in both cases as reference spectrum to validate the absolute wavenumber measurements. The using of methane spectrum as secondary standard of wavenumbers allows carrying out the well-posed comparison of FT and PA spectra.

2. High-Resolution Fourier Spectrometer

As it was mentioned above, measurements of the ethylene absorption spectrum were conducted with the use of a high-resolution Fourier transform spectrometer Bruker IFS 125HR. The internal tungsten light source was selected; the radiation was recorded with an InSb detector, cooled at liquefied nitrogen temperature. To measure the spectra, we have built a quartz cell 20 cm in length and 20 mm in diameter; its windows were made of CaF_2 . The cell was located in the spectrometer sample chamber. The FTS was pumped out up to a residual pressure of 0.015 Torr with a forevacuum pump, which significantly decreased the effect of atmospheric gases on the measured absorptions.

The ethylene absorption spectrum was recorded at room temperature and at a pressure of 19 Torr with a spectral resolution of 0.005 cm^{-1} and an optical path length of 20 cm. The gas with the 99.9% concentration of ethylene was used. The pressure was measured using the DVR-5 pressure gauge with an accuracy of less than 1 Torr.

To eliminate the temperature and pressure instabilities, which appeared just after filling the cell with the gas, measurements were conducted few hours after the filling. The signal-to-noise (S/N) ratio (expressed as the maximum signal amplitude divided by twice the RMS noise amplitude) was about of 700. It was obtained by the coaddition of 1600 interferograms.

TABLE 1: Calibrating factor.

$\nu_{\text{obs}}, \text{ cm}^{-1}$	$\nu, \text{ cm}^{-1}$ [10, 11]	C
6086.74696 (10)	6086.74541 (4)	0.999999745
6086.83242 (20)	6086.83070 (19)	0.999999726
6096.37435 (6)	6096.37273 (3)	0.999999734
6096.42606 (6)	6096.42439 (4)	0.999999726
6106.25353 (20)	6106.25205 (12)	0.999999757
6106.28556 (30)	6106.28412 (15)	0.999999764
6132.36374 (20)	6132.36199 (20)	0.999999714
		$C_{\text{av}} = 0.999999738$

When recording absorption spectra with the use of FTS, some shifts of line center positions from their true values are possible [12]. The principal causes of such shifts are due to instabilities of the radiation frequency of the reference laser and due to finite sizes of the infrared source and its radiation instability. To be corrected the shifts lead to the necessity of the frequency scale calibration.

The calibrating method used lies on the detection of some calibrating coefficients. It is shown in the literature (see, e.g., [12]) that there is some dependence between the Fourier-spectrometer-measured values of absorption line centers and the literature data:

$$\nu_{\text{cal}} = (1 + \alpha)\nu_{\text{obs}} = C\nu_{\text{obs}}, \quad (1)$$

where $\alpha \ll 1$, C is the calibrating factor.

In our work, the frequency scale was calibrated in the 6030–6200 cm^{-1} range using methane rovibrational lines belonging to $2\nu_3$ band and listed the HITRAN database [9]. To determine the calibrating factor, we used isolated absorption lines of methane (Table 1), the positions of centers of which were compared with data [10, 11].

The determination of absorption line-center positions in our work were performed by fitting a theoretical contour to the experimentally recorded line spectrum using the least square method. Voigt contour was used in the approximation. Examples of experimental and calculated methane spectra, including four absorption lines, are shown in Figure 1. Two of them, centered at 6096,4856 and 6096,5015 cm^{-1} are blended: therefore, they were not taken into account for the determination of the calibrating factor. Table 1 list the values of the methane absorption line-centers used in determining the calibrating factor. After averaging we have obtained the value $C_{\text{av}} = 0.999999742 \pm 1.8 \cdot 10^{-8}$. Figure 2 presents the record of the frequency-calibrated ethylene FTS spectrum within 6030–6210 cm^{-1} .

3. The Two-Channel OA Spectrometer with DL

The ethylene absorption PA spectrum was recorded by the two-channel laser spectrometer, basic elements of which are a narrow-band tunable DL with a controller (3, 4), two OA detectors (6), and the spectrometer's microcontroller (11). A specificity of the PA spectrometer is the simultaneous recording of two spectra of different gases and mixtures

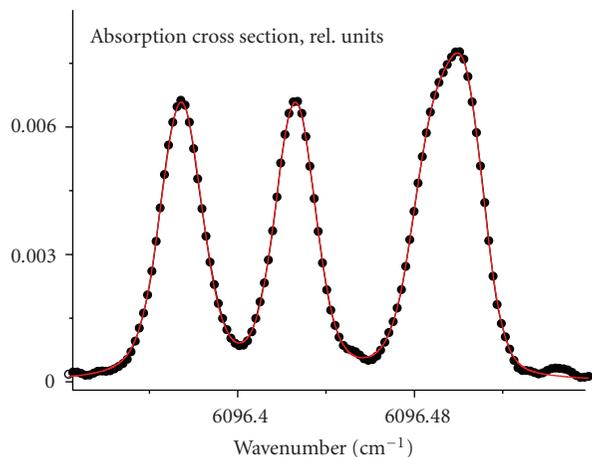


FIGURE 1: Methane absorption spectrum: the Voigt contour (solid line); experimentally recorded spectrum (dotted line).

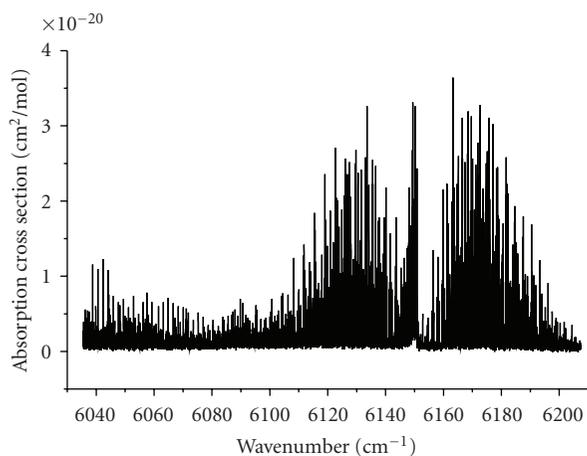


FIGURE 2: General view of the ethylene absorption spectrum recorded with the Fourier spectrometer.

TABLE 2: Specifications of the OA spectrometer.

Parameter	Value
Spectral interval, cm^{-1}	6020–6300
Spectral resolution, cm^{-1}	0.00033
Threshold sensitivity, cm^{-1}	$0.4 \cdot 10^{-6}$

under different thermodynamic conditions. In our measurements, one of PA detector (PAD) was filled with the mixture of ethylene and nitrogen and the second PAD with pure CH_4 at the pressure 5 or 7 Torr. The CH_4 absorption spectrum, known with a high accuracy, was used for the accurate determination of the DL radiation wavelength. Basic parameters of the spectrometer are presented in Table 2.

The spectrometer scheme is given in Figure 3. The measurement procedure and the spectrometer construction are presented in more detail in [13].

The TEC-100 semiconductor laser with an outer cavity (Sacher Laser Technik) generates the continuous single-frequency radiation within $6020\text{--}6300\text{ cm}^{-1}$ at a radiation spectrum width, not exceeding $\sim 10\text{ MHz}$ and an output power of $0.003\text{--}0.01\text{ W}$. The radiation power is controlled with a built-in photodiode and is modulated with a variable frequency optical chopper, Model 300C, SCITEC INSTRUMENTS [14].

The laser radiation frequency is controlled through a diffraction grating. The microscrew manual rotation of the grating allows the laser tuning to any wavelength from a given range, and the rotation with a piezoceramic element allows a smooth (free of mode jumps) retuning of the radiation frequency within the 3-cm range under the controller's management. The electric signal, controlling for the piezoceramic element, is produced by a 12-digit DAC, which varies the piezoceramic voltage between zero and 100 V following a given program. The minimal variation step is $\sim 0.024\text{ V}$, which corresponds to a step of $\sim 22\text{ MHz}$ (0.00073 cm^{-1}) of the laser radiation frequency tuning.

Measurements and the control for setting laser radiation to a given initial wavelength are made with a wavelength meter of WS-7 117 IR type (1), produced by the Angstrom company [15]. The absolute error of the initial wavelength measurements ($\Delta\nu/\nu$) does not exceed a value of 10^{-6} .

The control for the laser radiation frequency tuning in the program-controlled mode is performed with the use of the Fabry-Perot standard (2) (IT-28-30 with a base of 10 cm and a spectral dispersion range of 0.05 cm^{-1}). To eliminate the effect of jumps of the atmospheric air pressure on the value of the spectral dispersion range, the Fabry-Pérot standard is located in a pressure-tight housing, filled with the dry nitrogen at the atmospheric pressure.

As high-sensitive OA detectors (6) with a low level of acoustic noises, we used OAD with a cell in the form of the differential Helmholtz resonator (DHR) [13]. This resonator has a remarkable peculiarity: acoustic oscillations in DHR cells at the resonance frequency are in antiphase. Microphones, located in the cells, allow recording the difference between acoustic signals; therewith, the useful signal becomes duplicated, while the in-phase outer acoustic noise decreases by 1-2 orders of magnitude. The construction of the DHR with two capillaries, used by us, was totally symmetric and provided for a low level of the outer noise even in a gas flow. When the gas flow passed through the both DHR cells, the in-phased acoustic noise was generated in each of them, which further was subtracted by the differential amplifier. The threshold sensitivity of the DHR is $1 \cdot 10^{-9}\text{ cm}^{-1} \cdot \text{Hz}^{-1/2} \cdot \text{W}$.

A specially designed controller (11) is used in the device in order to automate measurements and to increase the accuracy and sensitivity. The 16-bit ADC ADS8725 (Texas Instruments) was incorporated into the controller for high-precision conversion of signals into digits from DHR microphones and from the laser power meter photodiode (9). To increase the device sensitivity, signals from both DHRs were detected synchronously in the computerized mode.

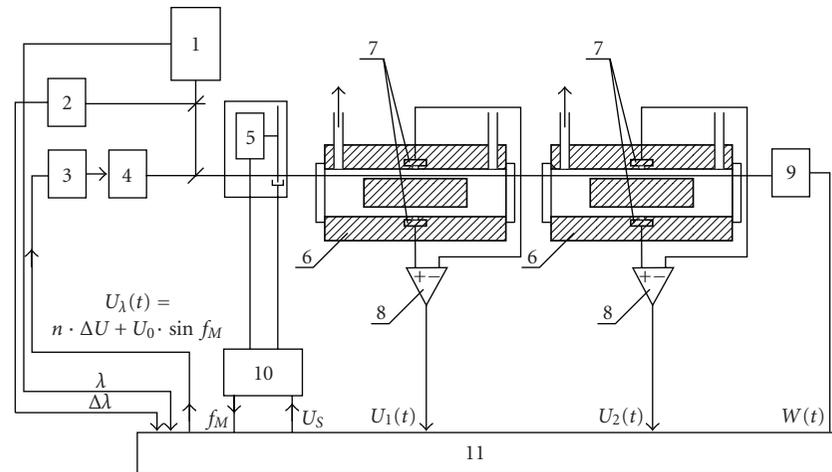


FIGURE 3: Schematic view of DOAS DL: wavelength meter (1); Fabry-Perot interferometer (2); DL controller (3); DL (4); modulator (5); PAD (6); Knowles 3027 microphone (7); differential amplifier (8); laser power meter (9); modulator's controller (10); spectrometer's controller (11); personal computer (12).

There is an analog output in the controller of the signal, controlling the laser wavelength tuning, which is necessary for realization of the spectrometer scanning mode. The device operation is possible both in the amplitude mode and in the mode of measuring the signal's derivative, which is formed from two signals: the retuning voltage and the sawtooth voltage of the laser beam modulation frequency. The management by the controller is realized through a serial port.

The controller intrinsic software is written in the Assembler language of microcontrollers of the AVR architecture. The calibrating and service software is written inside the LabVIEW 5.0 package medium and operates under Windows-XP, Windows-2000, and Windows-98 operation media. The on-screen user menu is presented in Figure 4.

Two first windows of the menu represent signal amplitudes of DHR with the pure methane and with the mixture of ethylene and broadening gas (nitrogen), respectively. The middle window shows the value of the laser radiation power and the next one—the Fabry-Perot interferometer transmission. The bottom window shows the laser-power-normalized signals from both DHRs. The panel of the control for laser parameters, the synchronous detector, and the input of initial parameters is to the left.

The smooth computer-controlled tuning of the DL radiation frequency is possible only in a narrow spectral range about 3 cm^{-1} , therefore, recording the spectrum throughout a given range was realized, using the piecewise continuous mode. In this connection, when uniting individual spectral fragments, some troubles appear. An absorption line with a known frequency should be present in each fragment. The ethylene absorption spectrum was recorded simultaneously with the methane absorption spectrum, and line-centers of methane absorption lines located in each narrow spectral range are used to obtaining the absolute frequency scale. Figure 5 presents a fragment of the pure methane absorption spectrum as compared to the calculated one. The

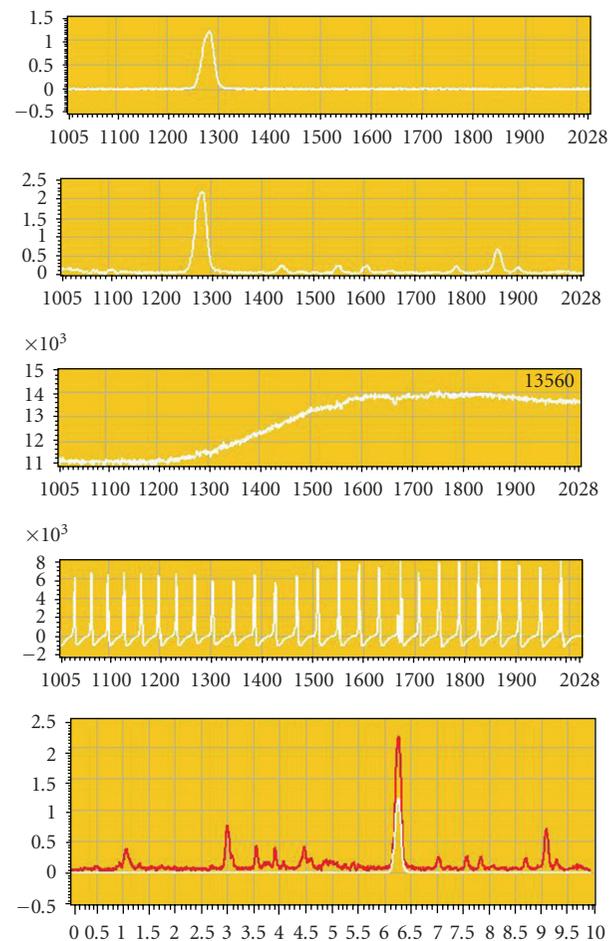


FIGURE 4: Menu of controlling and taking information from the two-channel spectrometer.

calculation was conducted, using the internet-information system "Spectroscopy of atmospheric gases" [16].

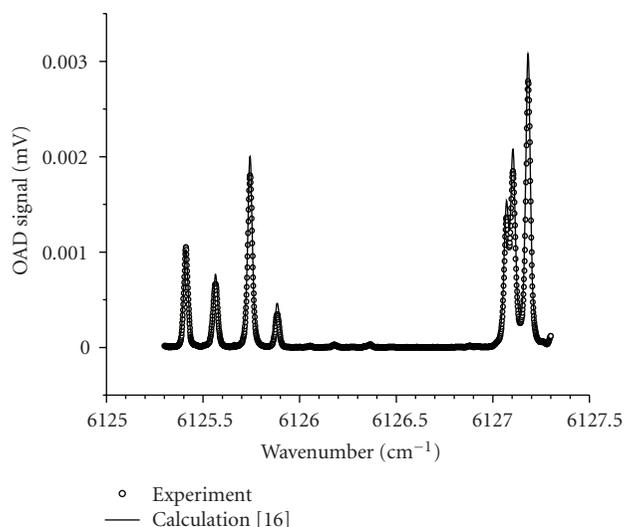


FIGURE 5: Experimental and calculated methane absorption spectra in the range of DL smooth radiation frequency tuning.

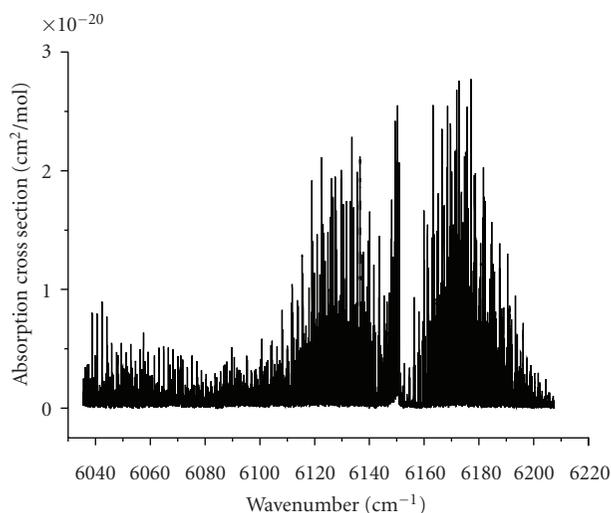


FIGURE 6: PA ethylene absorption spectrum.

Line center positions were estimated from the fitting of the recorded spectrum to the theoretical one. The estimation error was between 0.0005 (for isolated lines) and 0.004 cm^{-1} (for overlapping lines).

To increase the PAD sensitivity, measurements of the ethylene absorption spectrum were conducted for the mixture of ethylene-to-nitrogen ratio 1 : 70 at a mixture pressure of 31 Torr and a temperature of 293 K. The PAD calibration method and the estimation of the ethylene absorption cross-section are given in detail in [8].

Figure 6 shows the general schematic view of the OA absorption ethylene spectrum.

The recorded spectrum exhibits a complex structure; the absorption line density can reach 20 and more lines per inverse centimeter with a line FWHM of 0.01 cm^{-1} .

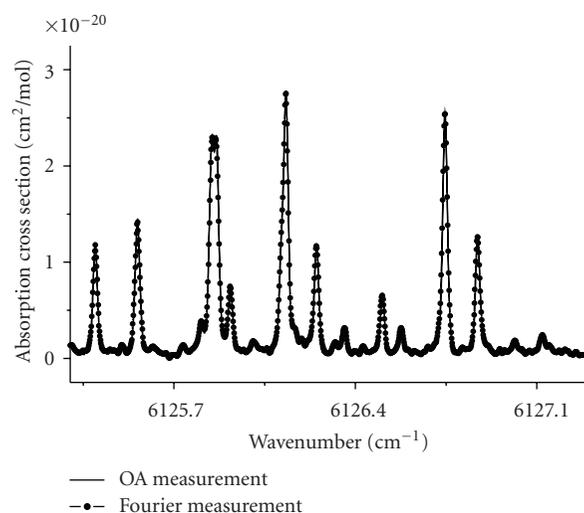


FIGURE 7: Comparison of ethylene absorption spectra within the 6125.3–6127.3 cm^{-1} range recorded with PA and FT spectrometers.

This significantly hinders the spectrum fitting, the determination of line center positions and absorption line intensities as well as increases errors in the determination of line-centers. We compared ethylene absorption spectra, obtained by two independent recording methods (Fourier transform and Photoacoustic) through imposing one of them on another. This way allowed the estimation of the coincidence of spectra throughout the range under study (6030–6200 cm^{-1}) with an error of about 0.0005 cm^{-1} . Figure 7 shows the comparison of spectra in one of the fragments.

4. Conclusion

The analysis of literature data of ethylene high resolution absorption spectrum [4–8] has shown the presence of differences in line-center positions and in absorption cross-sections which exceeded the measurement error. To verify the data presented in [8] the ethylene absorption spectrum in the 6035–6210 cm^{-1} range was recorded with the use of a high resolution FT spectrometer Bruker IFS 125HR (France, Institute Carnot de Bourgogne) [9]. The systematic inaccuracy in line-center positions on 0.025 cm^{-1} of these two data is observed. The causes of these differences are unclear yet. We have carried out comparative measurements of ethylene absorption spectra by two independent methods. For the frequency-scale calibration we have used the methane absorption spectrum, and the fitting of measurement results to the frequency scale was conducted by the methane absorption line-center positions given in the HITRAN database [10] and in the work [11].

By contrast to data from other authors [4–7, 9], the comparison between FT and PA spectra recorded in this study are in good agreement throughout the investigated range (6030–6200 cm^{-1}) with an error of about 0.0005 cm^{-1} .

Acknowledgments

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