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Research Article

Integrated Band Intensities of Ethylene ($^{12}C_2H_4$) by Fourier Transform Infrared Spectroscopy

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The integrated band intensities of ethylene ($^{12}C_2H_4$) in the 640–3260 cm^{-1} region were determined by Fourier transform infrared (FTIR) spectroscopy. The infrared absorbance spectra of the ν_7 and ν_{10}, ν_{12}, $\nu_7+\nu_8$, $\nu_6+\nu_{10}$, ν_{11}, and ν_9 and $\nu_2+\nu_{12}$ bands of ethylene recorded at a resolution of 0.5 cm^{-1} were measured at an ambient temperature of 296 K at various vapor pressures ranging from 3×10^{-5} to 1×10^{-3} atm to obtain respective Beer-Lambert's law plots. The measured integrated band intensities in cm^{-1}/cm atm were $S(\nu_9 \text{ and } \nu_2+\nu_{12}) = 112.20\pm0.24$, $S(\nu_{11}) = 55.35\pm0.14$, $S(\nu_{12}) = 41.22\pm0.30$, and $S(\nu_7 \text{ and } \nu_{10}) = 328.66\pm16.55$. In addition, the measured infrared band intensities of the $\nu_7+\nu_8$ and $\nu_6+\nu_{10}$ combination bands of ethylene are reported for the first time: $S(\nu_7+\nu_8) = 21.701 \pm 0.028$ cm^{-1}/cm atm and $S(\nu_6+\nu_{10}) = 2.568 \pm 0.025$ cm^{-1}/cm atm.

1. Introduction

Ethylene ($^{12}C_2H_4$), the simplest of all alkenes, is an important hydrocarbon. Terrestrially, it is a known tropospheric pollutant that affects the ozone concentration in the atmosphere [1]. It is produced by plants [2, 3], the incomplete combustion of fossil fuels [4], forest fires [5–7], volcanic emissions, and natural gas [4, 8]. As such, the measurement of ethylene concentration in the atmosphere is of great interest and importance. Beyond Earth, ethylene has been detected as a trace component of the atmospheres of the outer planets Jupiter, Saturn, Neptune [9–12], and the satellite Titan [13–18]. Ethylene has also been observed in circumstellar clouds IRC+10216 [19] and IRL618 [20]. The 10 μm band system of $^{12}C_2H_4$ which contains the strong ν_7 band as well as the ν_{10} and ν_4 bands is of particular interest to spectroscopists and astrophysicists as the region is being used for C_2H_4 remote measurements in the infrared range [21, 22].

Given the integrated band intensities of ethylene, it is possible to determine spectroscopically the concentration and distribution of ethylene in the atmosphere at any given temperature or pressure. Recent measurements of vibrational band intensities of $^{12}C_2H_4$ include the ν_7, ν_{10}, and ν_{12} bands [21–24] while Bach et al. [25] measured relative line intensities of the ν_{11}, $\nu_2+\nu_{12}$ and ν_9 bands. New data on the intensities and line positions in the ν_{12} band of $^{12}C_2H_4$ as reported by Rotger et al. [21] are included in the 2009 edition of the GEISA database [26] and in the HITRAN 2008 molecular spectroscopic database [27]. Also included in the HITRAN database [28] are intensities of the ν_7 [22], ν_9, and ν_{11} bands [29] of ethylene, and the calculated intensity ratio of the ν_7 band to the ν_{10} band of ethylene [30]. In this paper, we report the improved results of our laboratory measurements of the integrated band intensities of $^{12}C_2H_4$ between 640 cm^{-1} and 3260 cm^{-1} by Fourier transform infrared (FTIR) spectroscopy covering the following ethylene bands: ν_7 and ν_{10}, ν_{12}, $\nu_7+\nu_8$, $\nu_6+\nu_{10}$, ν_{11}, and ν_9 and $\nu_2+\nu_{12}$. To our knowledge, the measured integrated band intensities of $\nu_7+\nu_8$ and $\nu_6+\nu_{10}$ are reported for the first time. This work is part of our FTIR studies of the ethylene molecule and its isotopomers [31–34].

2. Experimental Details

The ethylene gas samples used in the experiments with a stated purity of 99.99% were purchased from Sigma-Aldrich in USA. All unapodized spectra were recorded at a resolution of 0.5 cm^{-1} in the 640–3260 cm^{-1} region using a Bruker IFS 125 HR Michelson Fourier transform spectrometer located at the Spectroscopy Laboratory of the National Institute of Education, Nanyang Technological University in Singapore. A globar infrared source together with a high-sensitivity liquid nitrogen cooled Hg-Cd-Te detector and KBr beamsplitter were used for all recordings. The spectra were collected at an ambient temperature of 296 K and at about 30 different vapor pressures in the 3×10^{-5} to 1×10^{-3} atm (0.03–1.00 mb) range as measured by a capacitance pressure gauge. An absorption length of 0.80 m was achieved by adjusting for four passes in the multiple-pass absorption cell with a 20-cm base path. A total of 100 scans were coadded to produce each spectrum of high signal-to-noise ratio. A background spectrum of the evacuated cell was recorded at the same resolution. The ratio of the $^{12}C_2H_4$ spectrum to the background spectrum yielded a transmittance spectrum with relatively smooth baseline. The transmittance spectrum was then converted to absorbance spectrum ($\ln(I_0/I)$) and the area for each band in the region was determined at different pressures using the OPUS 6 software.

3. Results and Discussion

The vibrational bands of pure ethylene vapor in the 640–3260 cm^{-1} wavenumber region are shown in the survey absorbance spectrum in Figure 1. The spectrum was recorded at a resolution of 0.5 cm^{-1} at a 4.56×10^{-4} atm vapour pressure and at an ambient temperature of 296 K. Figure 1 also shows the overlapping of the ν_{10} and ν_7 bands at the far right and of the ν_9 and $\nu_2 + \nu_{12}$ bands at the opposite end of the spectrum.

The integrated band intensity, $S(\nu)$ is given by the equation [35, 36]:

$$S(\nu) = \int_{\text{band}} k(\nu)d\nu = \frac{1}{pl}\int_{\text{band}} \ln\frac{I_0}{I}d\nu, \quad (1)$$

where p is the vapor pressure in the cell, l is the path length, and I_0 and I are the incident and transmitted intensities of light at frequency ν. To find $\int_{\text{band}} \ln(I_0/I)d\nu$, the absorbance area of each band in the ethylene spectrum was determined for different pressures. The band area (cm^{-1}) was then plotted against pressure (atm) and the integrated band intensities $S(\nu)$ in cm^{-1}/cm atm were determined from the gradient of each plot. The experimental gas path length (l) used in the calculation was 0.80 m. The procedure used in the determination of $S(\nu)$ is similar to that of Kagann and Maki [36]. In Figure 2, the Beer-Lambert's law plots are shown for the ν_9 and $\nu_2 + \nu_{12}$, ν_{11}, $\nu_6 + \nu_{10}$, and $\nu_7 + \nu_8$ bands of ethylene. Straight lines passing through the origin were accurately fitted with correlation coefficient R^2 ranging from 0.985 to 0.990.

Table 1 presents the results of the present work together with those of previous works [21, 22, 29, 35] for comparison.

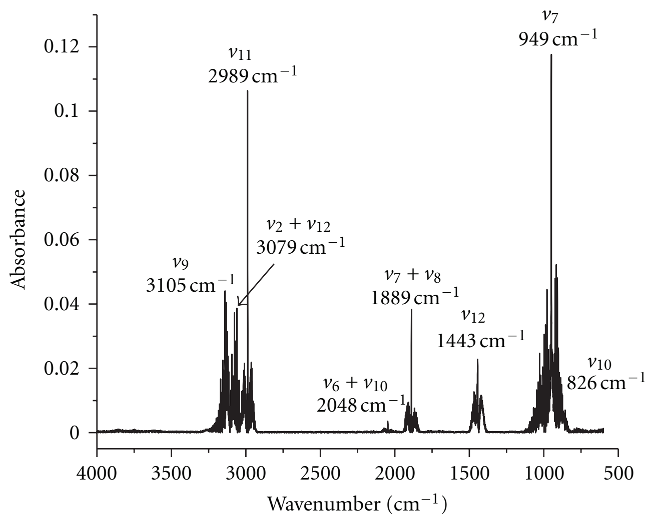


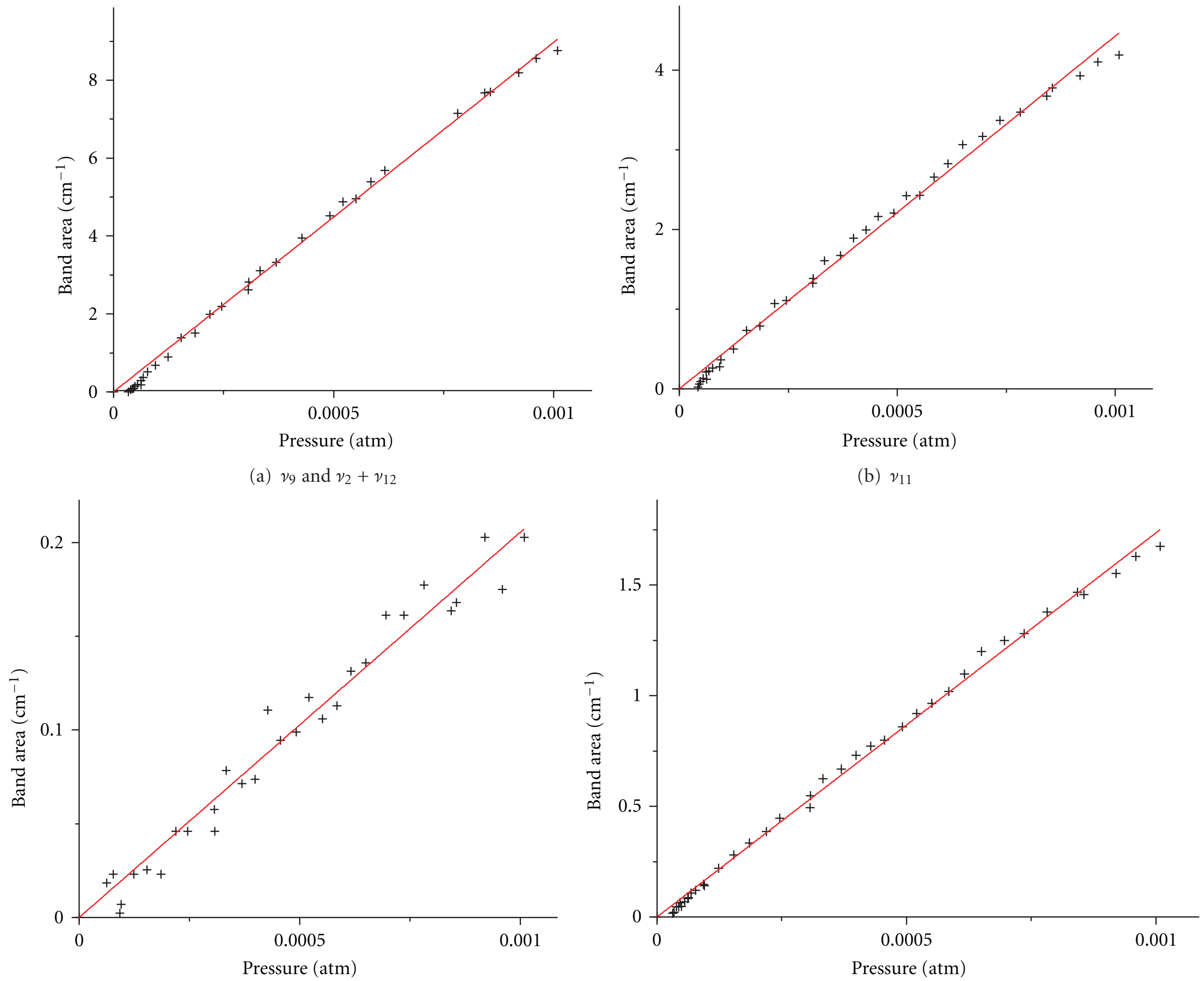
Figure 1: A survey FTIR absorbance spectrum of C_2H_4 collected at 0.5 cm^{-1} resolution at an ambient temperature of 296 K and at 4.56×10^{-4} atm vapor pressure in the 640–3260 cm^{-1} region.

Previously reported integrated band intensities of the ν_9 and ν_{11} bands of $^{12}C_2H_4$ were from Golike et al. [35]: $S(\nu_9) = 101 \pm 3\,cm^{-1}$/cm atm at band center $\nu_0 = 3105.5\,cm^{-1}$ and $S(\nu_{11}) = 54.9 \pm 0.3\,cm^{-1}$/cm atm at band center $\nu_0 = 2985.5\,cm^{-1}$. A more recent study [29] included in the HITRAN database [28] that involves 148 selected measurements in the 3 μm region of $^{12}C_2H_4$ gives the integrated band intensities of the ν_9 and ν_{11} bands as $S(\nu_9) = 82.52 \pm 0.86\,cm^{-1}$/cm atm at $\nu_0 = 3104.885\,cm^{-1}$ and$S(\nu_{11}) = 65.87 \pm 0.64\,cm^{-1}$/cm atm at $\nu_0 = 3012.436\,cm^{-1}$. In our work, since the ν_9 band closely overlaps with the $\nu_2 + \nu_{12}$ combination band, we could only determine the combined band intensity of $S(\nu_9$ and $\nu_2 + \nu_{12}) = 112.20 \pm 0.24\,cm^{-1}$/cm atm. The ratio of $S(\nu_9$ and $\nu_2 + \nu_{12})$ to $S(\nu_{11})$ calculated as 2.0 was found to be close to the value of 1.8 determined by Bach et al. [25] in their FTIR rotational analysis. For the isolated ν_{11} band, $S(\nu_{11}) = 55.35 \pm 0.14\,cm^{-1}$/cm atm at $\nu_0 = 2989\,cm^{-1}$ was determined in our work. These values, $S(\nu_{11})$ and ν_0, closely agree with those obtained by Golike et al. [35] but differ with those reported by Dang-Nhu et al. [29] (see Table 1). The discrepancy in the $S(\nu_{11})$ values obtained may be explained by the different band center used by Dang-Nhu et al. in their study. Their band center $\nu_0 = 3012.436\,cm^{-1}$ for the ν_{11} band of $^{12}C_2H_4$ is a few wavenumbers off from what Golike et al. [35] and our work had used which are close to what is reported in recent literature (~2989 cm^{-1}) [25, 37]. For the ν_{12} band, our result of $S(\nu_{12}) = 41.22 \pm 0.30\,cm^{-1}$/cm atm agrees well with the latest reported value of $S(\nu_{12}) = 41.16 \pm 0.50\,cm^{-1}$/cm atm [21] in the updated GEISA [26] and HITRAN [27] databases. For the first time, the integrated band intensities of the weak $\nu_6 + \nu_{10}$ and strong $\nu_7 + \nu_8$ combination bands have been measured. Moreover, high accuracy is shown in the values of $S(\nu_6 + \nu_{10}) = 2.568 \pm 0.025\,cm^{-1}$/cm atm and $S(\nu_7 + \nu_8) = 21.701 \pm 0.028\,cm^{-1}$/cm atm. The areas of the overlapping bands, ν_{10} and ν_7, and ν_9 and $\nu_2 + \nu_{12}$, were not separated and the integrated intensities

Table 1: The integrated band intensities $S(\nu)$ of $^{12}C_2H_4$ at 296 K in the 640–3260 cm^{-1} region.

Band assignment	Band centre ν_0 (cm^{-1})	Band region (cm^{-1})	$S(\nu)$ (cm^{-1}/cm atm)	
			Previous works	Present work
ν_9 and $\nu_2 + \nu_{12}$	3105 and 3079	3034–3260	$S(\nu_9) = 100 \pm 3$[a]	112.20 ± 0.24
			$S(\nu_9) = 82.52 \pm 0.86$[b]	
ν_{11}	2989	2920–3034	56.0 ± 0.3[a]	55.35 ± 0.14
			65.87 ± 0.64[b]	
$\nu_6 + \nu_{10}$	2048	1990–2100	—	2.568 ± 0.025
$\nu_7 + \nu_8$	1889	1820–1950	—	21.701 ± 0.028
ν_{12}	1443	1340–1540	41.16 ± 0.50[c]	41.22 ± 0.30
ν_7 and ν_{10}	949 and 826	640–1200	$S(\nu_7) = 321.69 \pm 0.36$[d]	329 ± 16
			$S(\nu_{10}) = 1.16 \pm 0.47$[d]	

[a]See [35]. Value adjusted for 296 K. ν_9 band center $\nu_0 = 3105.5\ cm^{-1}$ and ν_{11} band center $\nu_0 = 2989.5\ cm^{-1}$.
[b]See [29]. ν_9 band center $\nu_0 = 3104.885\ cm^{-1}$ and ν_{11} band center $\nu_0 = 3012.436\ cm^{-1}$. Included in HITRAN database [28].
[c]See [21]. Value adjusted for 296 K. Included in GEISA and HITRAN databases [26, 27].
[d]See [22]. Value converted to cm^{-1}/cm atm. Included in HITRAN database [28].



(a) ν_9 and $\nu_2 + \nu_{12}$

(b) ν_{11}

(c) $\nu_6 + \nu_{10}$

(d) $\nu_7 + \nu_8$

Figure 2: Beer-Lambert's law plots of C_2H_4 bands that were measured in the 640–3260 cm^{-1} region: (a) combined ν_9 and $\nu_2 + \nu_{12}$, (b) ν_{11}, (c) $\nu_6 + \nu_{10}$, and (d) $\nu_7 + \nu_8$.

of these bands are reported as combined (see Table 1). As expected, the strong ν_7 band has the largest band intensity in the region with very small contribution from the overlapping but weak ν_{10} band, $S(\nu_{10}) = 1.16 \pm 0.47\,\mathrm{cm}^{-1}/\mathrm{cm\ atm}$ [22]. Overall, our results which show good agreement with those from previous studies are more accurately determined.

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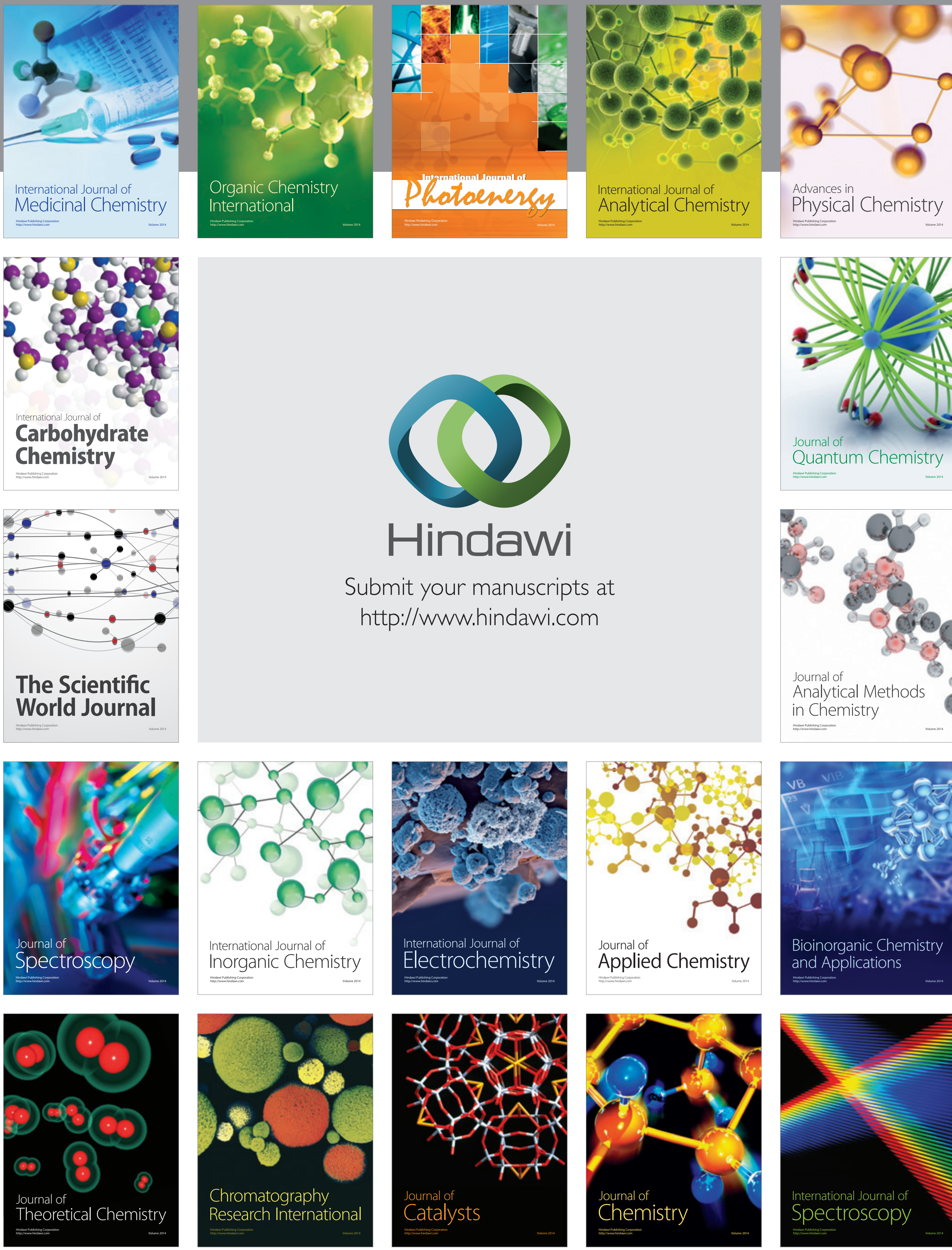
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