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Short Communication

In-situ ATR-IR investigation of methylcinnamic acid adsorption and hydrogenation on $\text{Pd}/\text{Al}_2\text{O}_3$

Xiaojing Sun, Christopher T. Williams*

Department of Chemical Engineering and NanoCenter, Swearingen Engineering Center, University of South Carolina, Columbia, SC 29208, United States

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ABSTRACT

The adsorption and hydrogenation of C = C in α -methylcinnamic acid in dichloromethane over the concentration range 2–16 mM have been studied on Al₂O₃ and Pd/Al₂O₃ using in-situ attenuated total reflection infrared (ATR-IR) spectroscopy. For Al₂O₃, the spectra reveal that the acid adsorbs both molecularly and dissociatively, while for 1 wt.% Pd/Al₂O₃ only the latter is observed. In the case of molecular adsorption, C = O stretching vibrations arising from adsorbed monomer (1710 cm⁻¹) and dimer (1684 cm⁻¹) species were observed. In the case of dissociatively adsorbed carboxylate, the typical asymmetric (1522 cm⁻¹) and symmetric (1378 cm⁻¹) vibrations are observed. No changes in adsorbed species were observed in the presence of solution-phase H₂ over alumina, whereas significant changes occurred for Pd/Al₂O₃. While bands associated with monomer/dimer and carboxylate species still persist on the surface in the presence of H₂, new vibrational features associated with adsorbed product (i.e., α -methylhydrocinnamic acid) are detected. The results demonstrate that the product is strongly adsorbed under hydrogenation conditions, which likely influences the catalytic performance of this system.

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1. Introduction

The importance of synthesis of chemicals containing one or more chiral centers has been appreciated and addressed in the manufacture of pharmaceuticals, agrochemicals, and fragrances for decades. For example, the three top-selling drugs for 2008 - Lipitor (atorvastatin calcium), Plavix (clopidogrel bisulfate) and Nexium (esomeprazole magnesium), with total sales of \$30 billion - were all single-enantiomer drugs [1]. The move toward enantiopure chemicals has been driven both by performance requirements and government regulations, as well as environmental concerns. While homogeneous catalytic asymmetric catalysis continues to progress rapidly, intrinsic drawbacks exist such as difficult (and expensive) catalyst separation and catalyst instability. Such issues may help to explain the relatively wide gap between R&D output from academics and industry versus commercial application [2]. In this respect, the eventual use of heterogeneous catalysts can offer several major advantages, including ease of catalyst separation, reduction of solvent usage, simplification of the synthetic route, and increased selectivity towards desired products. If optimized, these properties could result in significant economic and environmental benefits.

Cinchonidine-modified supported Pt-group metals are well-known and effective heterogeneous enantioselective catalysts, especially for the hydrogenation of prochiral C=O bonds. In contrast, chiral C=C bond hydrogenation with these catalysts has been less successful. The first study was apparently published in 1985, and involved prochiral cinnamic acid hydrogenation over Pd/C catalysts [3]. Largely over the past decade, there have been a number of studies [4-28] that have followed up on this initial work. The groups of Nitta [4-14], Bartok [15-18], and Baiker [19-28] have been the most active with the majority having explored hydrogenation of α , β - unsaturated C=C bonds adjacent to carboxylic acid groups with cinchonidine as modifier. It is suggested that cinchonidine (CD) and acids form a $CD(acid)_2$ complex during the enantioselective hydrogenation [26]. In addition, aromatic acids are more easily hydrogenated in polar solvents, as opposed to aliphatic acids that prefer non-polar environments. These (and other) studies of the cinchonidine-modified metal catalytic system have largely involved kinetics studies, as opposed to probing the surface molecular environment. In addition, the in-situ vibrational spectroscopic studies available have focused almost entirely on the cinchona alkaloid modifier interaction with the catalyst surface under different conditions [15,29,30].

The present communication reports an in-situ attenuated total reflection infrared spectroscopic study of the interaction of α -methylcinnamic acid with a Pd/Al₂O₃ catalyst. This molecule consists of a prochiral C==C bond located between COOH and phenyl groups (Fig. 1), and is a good model compound for the study of C = C hydrogenation in aryl substituted substrates. Overall, the conversion and enantioselectivity of this molecule is reported to be very low over cinchonidine-modified catalysts [15,16]. It was the aim of this work to begin to elucidate the surface molecular properties that may influence this behavior.

^{*} Corresponding author at: Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, United States. Tel.: +1 803 777 0143; fax: +1 803 777 8265.

E-mail address: willia84@cec.sc.edu (C.T. Williams).

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Fig. 1. Hydrogenation of α -methylcinnamic acid.

2. Experimental section

2.1. Materials

Dichloromethane (CHROMASOLV®), α -methylcinnamic acid (MCA, 99%) and α -methylhydrocinnamic acid (MHA, 98%) were obtained from Aldrich and used without further purification. The gas used for the experiments was ultrahigh purity hydrogen from National Welders Supply. PdCl₂ (Premion®, 99.999% (metals basis), Pd 59.5% min) and gamma aluminum oxide powder (99.5%, metal basis) were obtained from Alfa Aesar.

2.2. Catalyst preparation

1 wt.% Pd/ γ - Al₂O₃ catalyst was synthesized via wet- impregnation. Palladium chloride was used as the precursor and the support γ - Al₂O₃ powder had a mean particle size of 37 nm and a surface area of 45 m²/g. The catalyst prepared had around 50% dispersion based on H₂ chemisorption, with a mean palladium particle size of 2.6 nm, confirmed by high-resolution transmission electron microscopy.

2.3. ATR-IR Spectroscopy

An FTIR spectrometer (Nicolet 670) equipped with an ATR-IR accessory (SpectraTech) was used for these studies, as reported previously [31,32]. In the accessory there are two mirrors that allow the horizontal infrared light to be reflected vertically into the ATR-IR cell. Two holes in the bottom of the cell are designed to let the infrared light enter the ZnSe element sealed within the cell. A 60° zinc selenide (ZnSe) crystal (Spectra Tech) was selected for use as the ATR element upon which the catalyst film is deposited. The film was coated onto the ATR element using a suspension of 25 mg catalyst in 20 ml DI water. This mixture had been first placed in an ultrasonic bath overnight in order to obtain a uniform suspension. A thin layer of this suspension was spread into the ATR element and dried under a lamp. This procedure was repeated four times, giving an average film thickness of $10 \pm 2 \,\mu$ m, as found using optical microscopy (Olympus BX50 microscope and Simple PCI image analysis software by Compix).

The liquid solutions are kept in glass flasks (i.e., reservoirs) with magnetic stirring. Two separate reservoirs were used during the experiment without mixing between acid solutions and pure solvent (CH_2CI_2). Gas can be bubbled into the solution for hydrogenation experiments using an H_2 line attached to porous glass frit capped tube submerged in the reservoir. Pumps recycle the solution from the reservoirs, through the flow cell and back during the experiment. The flow path was altered by three-way valves that were automated and controlled using Labview (National Instruments). All experiments were carried out at room temperature and atmospheric pressure.

For acid adsorption experiments, pure solvent was flowed through the flow cell overnight prior to taking the background. At time zero, a spectral background was acquired and utilized for all the spectra taken during the experiment. Spectra were acquired continuously every ca 2 min during the experiment with 128 scans per spectrum using a resolution of 4 cm⁻¹. Pure solvent was continued for 1 hour, followed by 2 mM MCA in CH₂Cl₂ for 1 hour. Then the cycle is repeated, with solvent followed by acid solution, but for 16 mM acid and 8 mM acid, ending with a final solvent flush. For hydrogenation, after spectra were acquired in H₂-saturated pure solvent for 2 h, the flow was switched to H₂-saturated 0.016 M acid solution for 2 h. Finally the solution was purged with H₂-saturated solvent for 2 h. The adsorption and hydrogenation of α -methylhydrocinnamic acid (which is the product of the hydrogenation reaction) on 1 wt% Pd/Al₂O₃ was studied with ATR-IR to help interpret the hydrogenation spectra. In these experiments, a background was taken after bubbling hydrogen in solvent for 1 h, after which spectra in pure solvent were collected for 1 h. This was followed by 0.016 M product acid for 1 h, and finally pure solvent.

Vibrational assignments were assisted using spectral curve fitting to deconvolute overlapping peaks. Specific band assignments were aided by density functional theory (DFT) calculations on a single molecule in the gas phase using Gaussian 03 W, Revision B.02 [33] with the Becke three-parameter-Lee-Yang-Parr (B3LYP) method and the 6–31 G(d) basis set. The results were corrected by scaling factor 0.97.

3. Results and discussion

3.1. Reactant acid adsorption

The first step to study the hydrogenation of α -methylcinnamic acid is to understand the adsorption behavior of this reactant on the γ -Al₂O₃ support and Pd/Al₂O₃ catalyst. Prior to this, the ATR-IR spectra of the acid solution in contact with the bare ZnSe element were examined. The first plot in Fig. 2 shows typical spectra taken from acid solution in contact with the bare element as a function of the concentration profile described before. The seven spectra shown from the bottom to the top were the spectra taken at the end of each indicated experimental step. Two clear peaks are observed at 1715 cm^{-1} and 1685 cm^{-1} . From the literature [19], the 1715 cm⁻¹ peak is associated with C=O stretching from acid monomers, while the 1685 cm^{-1} peak is associated with acid dimer species. The small peak at 1492 cm^{-1} is assigned to the ring vibration, while peaks at 1448 cm^{-1} and 1407 cm^{-1} correspond to methyl group vibrations. Usually, the monomer acid is favored in very dilute solution in non-polar solvents, or in the vapor phase. Indeed, the relative sizes of the peaks change with concentration, showing that the dimer species is favored at higher concentrations. However, most importantly, these liquid phase peaks disappear completely upon switching to pure solvent; this confirms that there is no strong adsorption on the ZnSe surface.

Fig. 3 shows ATR-IR spectra obtained in the same fashion, but for an Al₂O₃ film. As can be seen, the peak intensities are increased and there are peaks remaining after removal of liquid-phase acid, suggesting that acid is adsorbed on the alumina. The peak associated with monomer C = O decreased, while the dimer-related peak increased, relative to the liquid phase. In addition, there is prominent peak at around 1640 cm⁻¹, which is assigned to C = C stretching [19]. Peaks around 1350 cm⁻¹ to 1500 cm⁻¹ were mainly associated with C–H bending vibrations in the methyl group, while the features from 1500 to 1600 cm⁻¹ arise from ring stretching vibrations. All of these assignments are shown in Table 1, and were made based on comparisons with characteristic frequency tables and the DFT calculation results. Fig. 4 shows that similar spectra were observed for the same experiment performed on the 1 wt.% Pd/Al₂O₃ sample, although some peak intensities are a little higher. Indeed, the peaks from 1500 to 1600 cm⁻¹ are clearly increased



Fig. 2. ATR-IR spectra for α-methylcinnamic acid (MCA) in contact with a bare ZnSe element. The spectra were acquired in order after exposure to a) pure solvent, b) 2 mM MCA, c) pure solvent, d) 16 mM MCA, e) pure solvent, f) 8 mM MCA and g) pure solvent. The plots on the right (h) are curve fitting for d). See text for details.

compared to Al_2O_3 alone, while the ratio of peaks found between 1600–1700 $\rm cm^{-1}$ and 1350–1500 $\rm cm^{-1}$ changed.

The spectra during adsorption experiments are complex and contain many overlapping peaks from a variety of sources, especially at the highest acid concentration of 0.016 M. To distinguish more clearly the peaks arising from bulk liquid and adsorbed species, the spectra were deconvoluted using least squared regression analysis. Before fitting could proceed, the peaks used to model liquid phase were determined. This was accomplished by fitting the IR spectra obtained from the bare element in 0.016 M acid, as shown in Fig. 3. The peaks at 1450, 1407, 1492, 1680, and 1715 cm⁻¹ can be readily assigned to liquid-phase acid. The resulting parameters for these liquid peaks were then used when fitting the IR spectra obtained in the presence of a film (i.e. Al_2O_3 or Pd/Al_2O_3). Initial inputs for surface adsorbed acid-related peaks were chosen based on the shape of the overall spectra and examination of residuals after subtraction of such liquid signals. The peaks from liquid-phase acid were modeled by pure Gaussian lineshapes, while the peaks from adsorbed species were modeled by a hybrid Lorentzian/Gaussian function. Several constraints were placed on the liquid peak parameters during the fitting routine within a given data set. The ratios, positions, and full widths at half maximum (FWHM) of the liquid peaks were kept constant, with only the intensity of the peaks allowed to vary. The same constraints were placed on the peak parameters for adsorbed acid on alumina when fitting the 1 wt.% Pd/Al₂O₃ spectrum. Finally, the intensities of any adsorbed acid peaks on Pd were allowed to vary while keeping other parameters constant. All the fitted spectra shown in the right plots in Figs. 2–4 were those taken for the highest concentration acid (0.0016 M) flowing through the cell. In these spectra, the red peaks are those arising peaks from liquid-phase acid, blue are those coming from adsorbed acid on alumina, and green are those observed on the Pd metal.

Based on this curve fitting, and vibrational frequencies calculated by DFT, peak assignments have been made and are summarized. Of



Fig. 3. ATR-IR spectra for α -methylcinnamic acid (MCA) adsorption on Al₂O₃. The spectra were acquired in order after exposure to a) pure solvent, b) 2 mM MCA, c) pure solvent, d) 16 mM MCA, e) pure solvent, f) 8 mM MCA and g) pure solvent. The plots on the right are curve fitting for d), with the curves indicated for spectral contributions from the h) liquid and i) adsorption on alumina. See text for details.

Table 1Vibrational peak assignments.

Vibrational mode	Peak assignment			
	Experimental			Calculation
	Bare ZnSe element	Al_2O_3	1 wt.% Pd/ Al ₂ O ₃	B3LYP/6-31 G(d)
C=O str. (monomer)	1716		1710	1738
C = 0 str. (dimer)	1684	1672		
C = C str.		1637	1632	1621
Ring str.		1554	1547	1566
Asymmetric COO ⁻ vib		1529	1522	
Ring symmetric vib.	1492	1491	1491	1483
Methyl group asymmetric C-H vib	1448	1450	1447	1457
Methyl group symmetric C–H vib	1407	1423	1403	1392
Symmetric COO⁻ vib	1386	1384	1378	
C-H vibration(H-C=C)			1346	1359

particular interest are the peaks ~1529 cm⁻¹ and ~1384 cm⁻¹, which are confidently assigned as asymmetric and symmetric COO⁻ vibrations base on the available literature [34,35]. The presence of these peaks shows that the reactant acid is dissociatively adsorbed on both the alumina and Pd surfaces. It is well known that different binding structures of carboxylates can be assigned based on the difference between asymmetric and symmetric COO⁻ vibration peaks. For example, a difference between 350 cm⁻¹ to 500 cm⁻¹ indicates a unidentate mode, 150–180 cm⁻¹ indicates a bridging bidentate mode, and 60–100 cm⁻¹ indicates a chelating bidentate. Thus, the bidentate bridging configuration, with the two oxygen atoms of the carboxylate bridging between two sites on the surface, is apparently favored under the conditions examined here.

Overall, considering the C=O stretching bands in these curve fitted plots, both monomer and dimer acid species exist in the bulk liquid phase. In contrast, only dimer is present on the alumina surface, and no significant dimer or monomer peaks are observed Pd. Thus, these spectra reveal that the acid adsorbs both molecularly and dissociatively on alumina but only dissociatively on Pd, at these conditions. It has been suggested previously [26] that on the cinchonidine (CD)-modified Pd surface, a CD(acid)₂ complex is present during the enantioselective hydrogenation. The present spectra obtained during adsorption suggest that such complexes may indeed be necessary to facilitate molecular adsorption on the surface.

3.2. Hydrogenation

After examining the adsorption of acid onto Al_2O_3 and Pd/Al_2O_3 catalyst, preliminary studies of α -methylcinnamic acid hydrogenation were performed. Based on the literature, this hydrogenation can be carried out effectively at room temperature and atmospheric hydrogen pressure, albeit with low activity. Fig. 5A and B show typical spectra for hydrogenation of 0.016 M acid on alumina and 1 wt.% Pd/Al_2O_3, respectively. The relevant spectra for reactant adsorption in the absence of H₂ at the same concentration are taken from Fig. 3. Finally, a spectrum is included for the adsorption of the product α -methylhydrocinnamic acid in dichloromethane directly after exposure of the catalyst to a 0.016 M concentration step for 1 h. It was expected that the Al_2O_3 would not show any surface reactivity towards hydrogenation. Indeed, Fig. 5A supports this supposition, since the spectrum taken in the presence of H₂-saturated acid is essentially identical to that obtained in H₂-free solution.

In contrast, Fig. 5B shows that in the case of catalyst, a very significant shoulder appears above 1700 cm^{-1} in the presence of H₂. Based on comparison with the spectrum obtained during product adsorption, this new peak can readily be assigned to the C=0 stretch of dimerized adsorbed product acid. Both the monomer and dimer C = O stretching frequencies for the product are blue shifted by about 50 cm⁻¹, due to the absence of an adjacent C=C bond. In addition, there is a broad feature around 1600 cm^{-1} , which can be assigned to ring stretching combined with the higher frequency C = C stretching peak from the reactant, which is still also adsorbed on both Pd and Al₂O₃. When the H₂-saturated acid was replaced by H₂-saturated pure solvent, the peak intensity decreased only slightly. Thus, once the product acid is formed on the surface, it apparently adsorbs strongly on the metal and/or support surface. Other than the C=C bond, the benzene ring is another possible unsaturated bond that can be hydrogenated. However, preliminary batch kinetic studies (not shown) of the same catalyst for this hydrogenation system at the same temperature and pressure indicate that only the C=C bond is hydrogenated under these conditions.



Fig. 4. ATR-IR spectra for α-methylcinnamic acid (MCA) adsorption on 1 wt.% Pd/Al₂O₃. The spectra were acquired in order after exposure to a) pure solvent, b) 2 mM MCA, c) pure solvent, d) 16 mM MCA, e) pure solvent, f) 8 mM MCA and g) pure solvent. The plots on the right are curve fitting for spectrum d), with the curves indicated for spectral contributions from h) liquid, i) adsorption on alumina, and j) adsorption on Pd. See text for details.



Fig. 5. ATR-IR spectra obtained during hydrogenation of MCA on alumina and 1 wt.% Pd/Al₂O₃. MCA and product (MHA) adsorption spectra acquired in separate adsorption experiments in the absence of H₂ are shown for comparison.

4. Conclusions

The adsorption of α -methylcinnamic acid in dichloromethane at room temperature on Al₂O₃ and 1 wt.% Pd/Al₂O₃ powder thin films was characterized by ATR-IR. While both monomer and dimer acid species are present in the liquid phase, the only molecular adsorption on Al₂O₃ was in dimer form. In contrast, there was essentially no observed molecular adsorption on the Pd surface. The presence of asymmetric and symmetric COO⁻ vibration peaks and their band separation indicated adsorbed bidentate bridging carboxylate species on both Al₂O₃ and Pd. Thus, this substituted acid adsorbs both molecularly and dissociatively on Al₂O₃, but only dissociatively on Pd. Introduction of solution phase hydrogen had no effect on the surface speciation on Al₂O₃ alone. In contrast, strongly adsorbed product was formed in the presence of Pd/Al_2O_3 , where it may reside on the metal and/or the support. Present studies are focused on elucidating the interaction of adsorbed acid with cinchonidine modifier in the presence and absence of solution-phase hydrogen, and correlating these measurements with observed reaction kinetics studies conducted under the same conditions.

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References

- IMS Health, Top 15 global products 2008, 2008 Global Prescription Sales Information, Top-line Industry Data, Press Room, 22.04.2009, 2009.
- A.M. Rouhi, Chiral chemistry, Chemical and Engineering News 82 (2004) 47–62.
 J.R.G. Perez, J. Malthete, J.C.R. Jacques, Academy of Sciences of the Paris Serie II
- 300 (1985) 169–172.
 [4] T. Sugimura, J. Watanabe, T. Uchida, Y. Nitta, T. Okuyama, Catalysis Letters 112 (2006) 27–30.
- [5] Y. Nitta, J. Watanabe, T. Okuyama, T. Sugimura, Journal of Catalysis 236 (2005) 164–167.
- [6] T. Sugimura, J. Watanabe, T. Okuyama, Y. Nitta, Tetrahedron-Asymmetry 16 (2005) 1573–1575.
- [7] Y. Nitta, T. Kubota, Y. Okamoto, Journal of Molecular Catalysis A: Chemical 212 (2004) 155–159.

- [8] Y. Nitta, T. Kubota, Y. Okamoto, Bulletin of the Chemical Society of Japan 74 (2001) 2161–2165.
- [9] Y. Nitta, Bulletin of the Chemical Society of Japan 74 (2001) 1971–1972.
- [10] Y. Nitta, Topics in Catalysis 13 (2000) 179–185.
- [11] Y. Nitta, T. Kubota, Y. Okamoto, Bulletin of the Chemical Society of Japan 73 (2000) 2635–2641.
- [12] Y. Nitta, Chemistry Letters 28 (1999) 635-636.
- [13] Y. Nitta, Y. Okamoto, Chemistry Letters 27 (1998) 1115-1116.
- [14] Y. Nitta, A. Shibita, Chemistry Letters 27 (1998) 161–162.
- [15] G. Szollosi, T. Hanaoka, S. Niwa, F. Mizukami, M. Bartok, Journal of Catalysis 231 (2005) 480–483.
- [16] G. Szollosi, S. Niwa, T. Hanaoka, F. Mizukami, Journal of Molecular Catalysis A: Chemical 230 (2005) 91–95.
- [17] K. Szori, G. Szollosi, K. Felfoldi, M. Bartok, Reaction Kinetics and Catalysis Letters 84 (2005) 151–156.
- [18] I. Kun, B. Torok, K. Felfoldi, M. Bartok, Applied Catalysis A: General 203 (2000) 71–79.
- [19] D. Ferri, T. Burgi, A. Baiker, Journal of the Chemical Society, Perkin Transactions 2 (2002) 437–441.
- [20] K. Borszeky, T. Burgi, Z. Zhaohui, T. Mallat, A. Baiker, Journal of Catalysis 187 (1999) 160–166.
- [21] K. Borszeky, T. Mallat, A. Baiker, Catalysis Letters 59 (1999) 95-97.
- [22] K. Borszeky, T. Mallat, A. Baiker, Tetrahedron-Asymmetry 8 (1997) 3745-3753.
- [23] M. Maris, T. Burgi, T. Mallat, A. Baiker, Journal of Catalysis 226 (2004) 393-400.
- [24] M. Maris, W.-R. Huck, T. Mallat, A. Baiker, Journal of Catalysis 219 (2003) 52-58.
- [25] W.-R. Huck, T. Burgi, T. Mallat, A. Baiker, Journal of Catalysis 205 (2002) 213-216.
- [26] W.-R. Huck, T. Burgi, T. Mallat, A. Baiker, Journal of Catalysis 200 (2001) 171–180.
- [27] W.-R. Huck, T. Mallat, A. Baiker, Journal of Catalysis 193 (2000) 1-4.
- [28] W.-R. Huck. T. Mallat, A. Baiker, Catalysis Letters 69 (2000) 129-136.
- [29] T. Mallat, E. Orglmeister, A. Baiker, Chemical Reviews 107 (2007) 4863-4890.
- [30] W.-R. Huck, T. Mallat, A. Baiker, Catalysis Letters 87 (2003) 241-247.
- [31] I. Ortiz-Hernandez, C.T. Williams, Langmuir 19 (2003) 2956-2962.
- [32] I. Ortiz-Hernandez, C.T. Williams, Langmuir 23 (2007) 3172-3178.
- [33] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Comperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
- [34] K. Dobson, A. McQuillan, Spectrochimica Acta Part A 56 (2000) 557–565.
- [35] J. van den Brand, O. Blajiev, P.C.J. Beentjes, H. Terryn, J.H.W. de Wit, Langmuir 20 (2004) 6308-6317.