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Dominance of eclipsed ferrocene conformer in solutions revealed by the IR spectra between 400 and 500 cm^{-1}



Feng Wang ^{a,*}, Narges Mohammadi ^a, Stephen P. Best ^b, Dominique Appadoo ^c, Christopher T. Chantler ^d

^a Department of Chemistry and Biotechnology, School of Science, Computing and Engineering Technologies, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia

^b School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

^c Far-IR and High Resolution FTIR Beamline, Australian Synchrotron, 800 Blackburn Road, Clayton, Vic, 3168, Australia

^d School of Physics, University of Melbourne, Parkville, Victoria, 3052, Australia

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ABSTRACT

A combined Fourier transform infrared (FTIR) spectra of ferrocene (Fc) and density functional theory (DFT) based quantum mechanical calculations confirmed the dominance of the eclipsed Fc conformer in the fingerprint region of 400–500 cm⁻¹ in solutions. Solution IR spectra of Fc measured in acetonitrile (ACN, $\varepsilon = 35.69$), dichloromethane (DCM, $\varepsilon = 8.93$), tetrahydrofuran (THF, $\varepsilon = 7.43$) and dioxane (DOX, $\varepsilon = 2.21$) show two well-defined bands in the 480-500 cm⁻¹ region with the higher-wavenumber band higher in intensity. The band profile agrees well with the earlier IR spectra of Lippincott and Nelson (1958) in tetrachloromethane solution as well as more recent measurement in dichloromethane solution of Duhović and Diaconescu (2013). DFT based quantum mechanical calculations predict that the eclipsed (D_{5h}) Fc conformer is lower in energy than the staggered (D_{5d}) conformer and that the room-temperature solution spectrum of Fc is dominated by that of the D_{5h} fc conformer which resulted in switch of the IR profile patterns in 400–500 cm⁻¹, from low-wavenumber band higher in intensity in solutions. It further suggests that the effects of solvents on the IR spectra of Fc in this region are small and the solvent model effects are also small for the IR spectrum in the region of 400–500 cm⁻¹ of Fc.

1. Introduction

Since its discovery some fifty years ago (Kealy and Pauson, 1951), dicyclopentadienyl iron (FeCp₂ or Fc) continues to be the focus of many studies in its own right and in its relation to the metal complexes of substituted cyclopentadienyl (Cp) and other cyclic derivatives. Exploitation of its well-defined redox behaviour, and ease of derivatization (Long, 1998) have resulted in a broad range of Fc derivatives which have found key roles in homogeneous catalysis, polymer chemistry, molecular sensing, and nonlinear optical materials (Yamaguchi et al., 1998), organic solar cells (OSC), as well as biological applications (Osella et al., 2000; Fouda et al., 2007).

The ground-state conformation of the two parallel cyclopentadienyl rings of Fc, eclipsed (D_{5h} symmetry) or staggered (D_{5d} symmetry) is surprisingly difficult to resolve unambiguously, this being due to the

https://doi.org/10.1016/j.radphyschem.2021.109590 Received 22 March 2021; Accepted 26 May 2021 Available online 11 June 2021 0969-806X/© 2021 Elsevier Ltd. All rights reserved. small difference in energy between the rotameric forms and the small energy barrier between these forms (Cotton and Wilkinson, 1988; Mohammadi et al., 2012). This small rotational energy barrier, and attendant dynamic behaviour, challenges in the experimental studies of Fc since its discovery in 1951 (Kealy and Pauson, 1951). The debate on the most stable conformer of Fc, whether it is the eclipsed (D_{5h}) or the staggered (D_{5d}), with both experimental and other information (Wilkinson et al., 1952; Bohn and Haaland, 1966; Fischer, 1952), has been continuing without conclusive evidences until our ground-breaking study of Fc using IR spectroscopy (Mohammadi et al., 2012). A few years after the discovery of Fc, Lippincott and Nelson, 1953, 1955, 1958 reported the first infrared (IR) measurements. Notwithstanding the quality of the early measurements, the IR spectra of Fc were assigned to the staggered (D_{5d}) Fc conformer (Lippincott and Nelson, 1958), this being based on the interpretation of the crystal structure. Subsequent

^{*} Corresponding author. *E-mail address: fwang@swin.edu.au* (F. Wang).

reinterpretation of the X-ray structure in terms of statically or dynamically disordered D_{5h} Fc (Dunitz, 1995)] is also consistent with the vibrational spectra as reflected by normal coordinate analysis of Fc (D_{5h}) (Brunvoll et al., 1971). It is important to note that the predicted number of IR and Raman-active modes is the same for both staggered (D_{5d}) and eclipsed (D_{5h}) conformers of Fc.

Detailed structural understanding of the Fc conformers is very important as Fc derivatives may inherit particular properties which only exist in a particular conformer (Duhović and Diaconescu, 2013; Yamaguchi et al., 2007). For example, additional ligands coordinating to the metal and the Cp rings while maintaining certain symmetry is preferred for a particular geometry of Fc conformer (Duhović and Diaconescu, 2013; Cooper et al., 2011; Gryaznova et al., 2010). Design of synthesis pathways and understanding of the mechanics and reaction dynamics of the Fc derivatives require detailed information of the structure, symmetry and properties of the Fc conformers. The stability of eclipsed and staggered conformers of Fc has been a challenge issue and both structures were discussed in textbooks (Mehrotra, 2007; Veera, 1998; Atkins et al., 2010). A number of articles such as Coriani et al. (2006), Roy et al. (2008), Gryaznova et al. (2010) and Bean et al. (2011) have well documented the history and current status of the Fc studies.

Properties of the staggered and eclipsed conformers of Fc are not markedly different due to the shape of the conformers (both contain D_5 subsymmetry). The differences between most of the calculated properties of the Fc conformers are either zero or too small to differentiate (e. g., within the error of the methods), such as dipole moment and rotational constants (Mohammadi et al., 2012). This underlies why previous conclusions regarding the conformation of Fc are qualified or contradictory (Wilkinson et al., 1952; Bohn and Haaland, 1966; Fischer, 1952). Despite the one to one correspondence of the form of the IR-active modes for the D_{5h} and D_{5d} conformers, calculations of the IR spectra reveal a predicted signature of the different conformers (Mohammadi et al., 2012; Lippincott and Nelson, 1958) and it is timely to review the assignment of the observed IR spectra to the staggered (D_{5d}) conformer of Fc (Lippincott and Nelson, 1958).

Literature reveals that infrared (IR) spectral simulations of Fc (Lippincott and Nelson, 1953, 1958; Duhović and Diaconescu, 2013; Mohammadi et al., 2012; Gryaznova et al., 2010; Best et al., 2016; Wang and Vasilyev, 2020; Trevorah et al., 2020) that the DFT methods can be employed to interpret the measured IR spectra of Fc. However, the basis sets employed in the DFT models (Duhović and Diaconescu, 2013; Gryaznova et al., 2010) were not particularly suitable to the iron atom of Fc, the simulated IR spectrum of Fc needed scaling factors to fit the measurements (Duhović and Diaconescu, 2013; Gryaznova et al., 2010; Trevorah et al., 2020). As a result, the simulated Fc IR spectra may be useful for interpretation but hardly suitable for prediction purposes for dynamic systems. In a combined experimental and theory study, we further revealed (Best et al., 2016) that, owing to population of higher vibrational levels of the reaction coordinate the IR spectra of both rotameric forms are needed to calculate to temperature-dependence of the IR spectrum. This approach was shown to allow the self-consistent interpretation of the IR spectra of Fc in wax (solid) solution, CCl₄ solution and the gas phase, where in each case the eclipsed conformer of Fc is lowest in energy, but that the relative energies of the D_{5h} and D_{5d} forms is phase-dependent (Best et al., 2016) and temperature dependent (Wang and Vasilyev, 2020). Most important, if the energy difference between the D_{5h} and D_{5d} forms is larger than *ca*. 10 kJ mol⁻¹ then the RT spectrum will be dominated by the more stable form.

The DFT based Fc study (Mohammadi et al., 2012) suggested while there are only small differences in the calculated wavenumbers of the remaining normal modes for the D_{5h} and D_{5d} conformers, the spectral splitting within the IR region of 480–500 cm⁻¹ provides a means of distinguishing between the eclipsed and staggered Fc conformers. There are two vibrations of Fc in this region, one dominated by the translation of the Fe atom between the Cp rings (Fe translation), the other is best described as a tilting of the Cp rings towards each other and a translation of the Fe atom normal to the tilt axis of the Cp rings (Cp tilt). Only the latter of these modes is sensitive to the relative conformation of the Cp rings, consequently there is a difference in the relative energies of the two normal modes according to whether Fc has a D_{5h} or a D_{5d} geometry (Mohammadi et al., 2012). Importantly, there is a difference in the relative intensities of these modes which can be used to assist the analysis. For the D_{5h} conformer the more intense Cp-tilt mode is higher in wavenumber and there is a significant energy difference between the two modes (8-10 $\mbox{cm}^{-1})$ whereas for the D_{5d} form the two modes are nearly coincident (within 2 cm⁻¹). (Mohammadi et al., 2012). These signatures provide a means of using the IR measurements to identify whether there is a single conformer or a mixture of the two forms. The DFT based B3LYP/m6-31G(d) model were shown to simulate accurately the IR spectra of Fc without scaling, if used with an appropriate basis set (Mitin et al., 2003). It was shown that the central Fe atom of the sandwich compound plays a significant role (Mohammadi et al., 2012) and the modified 6-31G(d) basis set, i.e., m6-31G(d) (Mitin et al., 2003) is so far the most appropriate basis set for accurately modelling the complexes containing Fe.

In the present study, we provide a combined study of DFT calculations with FTIR experimental measurements in a range of solvents, in order to explore the impact of the environment on Fc conformation.

2. Experimental details and computational methods

Infrared (IR) spectra of Fc dissolved in non-polar solvents such as acetonitrile (ACN, $\epsilon=35.69$), dichloromethane (DCM, $\epsilon=8.93$), tetrahydrofuran (THF, $\epsilon=7.43$) and dioxane (DOX, $\epsilon=2.21$) were obtained using a Bruker Tensor 27 FTIR and a conventional solution cell fitted with KBr windows and a 100 μm spacer. A resolution of 1 cm-1 was used for all measurements. Concentrated solutions were prepared in each case and these spectra were compared with those obtained from the corresponding solutions diluted by factors ranging between 2 and 4 (Fig. 4). No significant concentration-dependent variation in the band profile was observed.

The optimized geometries of Fc eclipsed and staggered conformers were obtained using the B3LYP/m6-31G(d) model (Mitin et al., 2003). The DFT model is the same model in our previous study of Fc in gas phase (Mohammadi et al., 2012). This m6-31G(d) basis set incorporates necessary diffuse d-type functions for the Fe transition metal, so that it ensures a better performance than the conventional 6-31G(d) basis set for the iron atom of Fc, by providing a more appropriate description for the important energy differences between the atomic $3d^n4s^1$ and $3d^{n\cdot1}4s^2$ configurations (Martin et al., 2009). The present IR spectral simulations of the Fc conformers use the same model of B3LYP/m6-31G (d) in the solvents *without any scaling*.

As the IR spectra of Fc were measured in solutions, a number of implicit solvent models were employed in the simulations. Continuum solvation methods such as polarizable continuum model (PCM) or dielectric polarized continuum model (D-PCM which neglects the volume polarization) (Cossi and Barone, 1998), the conductor PCM (C-PCM, which approximates the volume polarization) (Cossi et al., 2003; Barone and Cossi, 1998) and the solute molecule density (SMD) model (Marenich et al., 2009) were employed in the IR spectral simulations. Geometry optimization calculations of Fc were performed for each such calculation, respectively, followed by vibrational frequency calculations. All calculations are performed using the Gaussian09 computational chemistry package (Gaussian 09 et al., 2009).

3. Results and discussion

Fig. 1 shows the analysis of the Fc IR spectrum in the acetonitrile (ACN, $\varepsilon = 35.69$) solution in the region of 400–1200 cm⁻¹. Five major spectral peaks (four bands) are measured in this region as given in Fig. 1 (a). The four measured major peaks (five bands) of Fc are analysed (Voigt fits) at 480.28 \pm 0.05 cm⁻¹ (Int: 0.12 \pm 0.001) and 496.25 \pm



Fig. 1. The measured FTIR spectrum of ferrocene in ACN solution (a) and Voigt fits for 4 bands (5 peaks) in the region of 400–1200 cm ⁻¹ (b₁-b₄).



Fig. 2. Measured FTIR spectra of ferrocene in the region of $400-1200 \text{ cm}^{-1}$ in a number of solvents at room temperature.

 0.03 cm^{-1} (Int: 0.19 ± 0.001) in Fig. 1 (b₁), $823.69 \pm 0.03 \text{ cm}^{-1}$ (Int: 0.20 ± 0.002) in Fig. 1 (b₂), at $1006.60 \pm 0.02 \text{ cm}^{-1}$ (Int: 0.16 ± 0.001) in Fig. 1 (b₃), and $1107.60 \pm 0.02 \text{ cm}^{-1}$ (Int: 0.25 ± 0.002) in Fig. 1 (b₄). Table 1 summarises the FTIR spectral information, including positions,

height of intensities and full width at half maximum (FWHM) etc. The intensity ratio of the measured major spectral peaks in the ACN solution from 400 to 1200 cm⁻¹ is 1:1.58:1.71:1.38:2.14, which is in good agreement with the recent IR measurement of Fc in DCM solution which is given by 1 : 1.39: 1.53 : 1.33: 1.55 (Duhović and Diaconescu, 2013) and this is in good/fair agreement with the calculated intensities in this solvent.

Fig. 2 compares the FTIR spectral region of 400–1200 cm⁻¹ in solvents at room temperature. The FTIR spectra were recorded non-polar solvents such as acetonitrile (ACN, $\varepsilon = 35.69$), dichloromethane (DCM, $\varepsilon = 8.93$) and tetrahydrofuran (THF, $\varepsilon = 7.43$). As seen in this figure, the spectra all exhibit four major peaks at ca. 480-500 cm⁻¹, 820 cm⁻¹, 1010 cm⁻¹ and 1100 cm⁻¹. The present FTIR spectra in solutions consistently show excellent agreement with the Fc IR spectrum of Duhovic and Diaconescu in the DCM solution (Duhović and Diaconescu, 2013) as well as the early IR spectrum of Lippincott and Nelson (1958) in chloroform solution (CCl₄) at room temperature.

Table 2 reports the Fc IR spectral peak positions in the solutions and compares with other experiment measurements and calculations in 400–1200 cm⁻¹. The present experimental measurements in different non-polar solvents consistently agree with available IR measurements in solutions in this region. For example, the IR spectral peak positions in the dichloromethane (DCM) solution were measured as 478 cm⁻¹ and 494 cm⁻¹, 822 cm⁻¹, 1004 cm⁻¹ and 1106 cm⁻¹ in a recent study (Duhović and Diaconescu, 2013), whereas the present measurement reports as 478 cm⁻¹ and 495 cm⁻¹, 820 cm⁻¹, 1005 cm⁻¹ and 1107 cm⁻¹, accordingly, almost exactly reproduce all IR spectral peak positions in the region of 400–1200 cm⁻¹. In addition, our experimental results show that the positions of the spectral peaks in the solvents are almost identical, which are consistently reported within ± 3 cm⁻¹, which indicates that solvent effects to the IR spectra of Fc are small and negligible, i.e., the IR spectra of Fc are insensitive to a change in the



Fig. 3. The measured IR spectrum (middle panel) of Fc in acetonitrile (ACN) solution with the simulated infrared spectra of the eclipsed (D_{5h} , top panel) and the staggered (D_{5d} , bottom panel) conformers of Fc in the region of 400–1200 cm⁻¹. The spectrum clearly indicates the dominance of eclipsed Fc in this solution.

polarity of the solvent.

To further explore the relative importance of the D_{5h}/D_{5d} conformations, Fig. 3 compares the measured FTIR spectrum (middle panel) of Fc in the acetonitrile (ACN) solution with the simulated IR spectra of the D_{5h} (top panel) and D_{5d} (bottom panel) conformers of Fc in the region of 400–1200 cm^{-1} . The simulated IR spectra were obtained using the B3LYP/m6-31G(d) model without scaling and shifting. In the simulation, the implicit solute molecular density (SMD) model (Marenich et al., 2009) is applied. Aside from the 400-500 cm^{-1} region, there is a general agreement between the measurement and calculated spectra of both conformers is observed. For example, in both Fc conformers, the major FTIR spectral peaks in the measurement (middle panel) are reproduced by the simulations. For example, the measured peak positions are given at 480 cm^{-1} /496 cm^{-1} , 823 cm^{-1} , 1006 cm^{-1} and 1107 cm^{-1} in the ACN solution. In the simulated IR spectrum of the D_{5h} Fc conformer in the same solution, these spectral peaks are given as $467 \text{ cm}^{-1}/484 \text{ cm}^{-1}$, 852 cm^{-1} , 1027 cm $^{-1}$ and 1133 cm $^{-1}$, accordingly, without any scaling and shifting. These IR peaks of the D_{5d} Fc conformer, on the other hand, are given by 458 cm⁻¹ (only one peak, as they are not resolved), 854 cm⁻¹, 1029 cm⁻¹ and 1134 cm⁻¹, accordingly, under the same conditions.

As discussed earlier the spectral features in the region of 400–500 cm^{-1} provide a signature of the Fc conformation (Mohammadi et al.,



Fig. 4. The measured FTIR spectra in the solutions of high and low concentrations in the IR fingerprint region of $400-600 \text{ cm}^{-1}$.

Table 1

Voigt fits (Lorentzian-Gaussian) of the FTIR spectra measured of ferrocene in ACN solution.

Solvent = ACN	υ_1	v_2	v_3	υ_4	v_5
Position	480.28	496.25	823.69	1006.60	1107.60
	± 0.05	± 0.03	± 0.03	± 0.02	± 0.02
Intensity	0.12	0.19	0.20	0.16	0.25
	± 0.001	± 0.001	± 0.002	± 0.001	± 0.002
FWHW	8.91	8.09	11.79	7.67	3.21
GL	0.47	0.27	0.66	0.8	0.52

2012) and the observed spectra are clearly consistent with the D_{5h} conformer being significantly lower in energy (>ca. 10 kJ mol⁻¹) than the D_{5d} form. In this case the two bands are well separated and are easily resolved and should be apparent from the earliest measurements (Lippincott and Nelson (1958, 1953) and Duhovic and Diaconescu (Duhović and Diaconescu, 2013)). Fig. 3 combines the experimental results with theory to confirm that only the IR spectral peak(s) of the D_{5h} Fc conformer in the region in 400–500 cm^{-1} gives two distinct peaks with a more intense peak at a higher wavenumber (i.e. 495 cm^{-1}) and a less intense peak at a lower frequency (i.e. 479 cm^{-1}). The staggered Fc conformer, however, does not show such the spectral splitting in this region, in agreement with our previous study in gas phase (Mohammadi et al., 2012). The insensitivity of the higher-wavenumber modes to Fc conformation reflects the form of those normal modes, where the vibrations near 845 cm^{-1} , 1032 cm^{-1} and 1141 cm^{-1} are assigned to C–H out of plane, C-C-H bend and Cp breathing (one Cp shrinks, one Cp expands) vibrations, respectively, in agreement with literature Table 2

Comparison of the n	neasured Fc spectral	peak	positions in	various solv	vents and	available e	xperiment and	calculations.
			•					

	This Work ^a						Ref. (D 2013)	uhović and Diaconescu,	Ref. (Gryaznova et al., 2010)	Ref. (Lippincott and Nelson, 1958)	
_	Expt.		B3LYP/m6-31G(d)		Expt. B3LYP/6-31G* ^b		B3LYP/Type-I	Expt.			
	ACN	DCM	THF	DOX	DOX ^a	Gas (Mohammadi et al., 2012)	DCM	Gas	Gas	CCl ₄	Gas
v_1	480	478	479	479	471	471	478	480	470	478	480
v_2	496	495	495	495	489	488	494	510	473	492	496
υ_3	823	820	820	821	845	844	822	844	825	811	816
v_4	1006	1005	1005	1006	1033	1035	1004	1036	1017	1002	1012
v_5	1107	1107	1108	_C	1141	1141	1106	1140	1141	1108	1112

^a DFT model: SMD-B3LYP/m6-31G(d).

^b A scaling factor of 0.95 was employed in the calculations in Ref (Duhović and Diaconescu, 2013) and private communications (2013).

 $^{\rm c}$ The spectrum cut off in this solution was after 1100 cm⁻¹ as the measurement in this solution concentrated in the region under 1000 cm⁻¹.

(Mohammadi et al., 2012; Lippincott and Nelson, 1958; Gryaznova et al., 2010). It is noted in Fig. 3 that the calculated spectral peaks red-shift (i.e. smaller than the measured) in the region of 400–500 cm⁻¹ but blue shift (i.e. larger than the measured) in the region of above 500 cm⁻¹ from the measurements.

The vibrational frequencies produced by quantum mechanical calculations are often multiplied by a scale factor (in the range of 0.8–1.0) (Gryaznova et al., 2010; Baker et al., 1998; Katsyuba et al., 2001; Selvam et al., 2010, 2011; Chen et al., 2010) to better match experimental vibrational frequencies. This scaling compensates the approximation in electronic structure calculations and anharmonicity of the potential energy surface. The vibrational frequencies are calculated by the second derivative of the potential energy surface with respect to the atomic coordinates and the anharmonicity causes the vibrational energy levels to be more closely spaced. As a result, the scaling factor is method dependent (Irikura et al., 2005).

For the current calculations of Fc, the scaling factor for the Fe–C motions is much closer to 1 (1.02) than previous calculations which required a scaling factor as large as 1.25 (Gryaznova et al., 2010) and this reflects the use of a more suitable m6-31G(d) basis set to calculate vibrational frequencies of Fe–C motions. Table 3 compares the measurements and calculations for the spectral peaks of the eclipsed Fc in different solutions. The largest error is within 4% between the measurements and calculations in the region of 400–1200 cm⁻¹, indicating that the theoretical model is sufficiently accurate for the Fc conformers. The red shift (by colour) for the Fe related vibrations and the blue shift for other vibrations are apparently shown in this table.

The present study will concentrate on IR spectra of the D_{5h} Fc in the region of 400–500 cm⁻¹, as the most noticeable feature of the FTIR spectra in Figs. 2 and 3 is the spectral peak splitting in the region of approximately 480–500 cm⁻¹ in all solutions. The major peak locates at 495 cm⁻¹ whereas the minor peak locates at 479 cm⁻¹, with a measured spectral splitting of approximately 16 cm⁻¹ in the ACN solution. The splitting of the two bands agrees well with the earlier IR measurement of Lippincott and Nelson (1958), in which the spectral peaks located at 492 cm⁻¹ and 478 cm⁻¹ in chloroform solution with a spectral splitting of 14 cm⁻¹, and with the recent FTIR measurement at 478 cm⁻¹ and 494 cm⁻¹ in DCM solution with a splitting of 16 cm⁻¹ of Duhovic and

Diaconescu (Duhović and Diaconescu, 2013). Note that the present IR calculations do not use any scaling whereas the calculated IR spectra of Duhovic and Diaconescu (Duhović and Diaconescu, 2013) employed a scaling factor of 0.95.

In Fig. 4, the FTIR measurements in the solutions are presented in high and low concentrations in the IR region of 400–600 cm⁻¹. The FTIR spectra do not exhibit apparent solvent dependent changes nor concentration dependent changes. In particular, the spectral peak positions in the solvents, such as DCM, THF and DOX which have small dielectric constants (i.e., $\varepsilon < 10$), are almost identical. Fig. 4 also shows that the concentration of the solutions does not change the positions of the spectral peaks with exception for the intensities. That is, the red spectra in Fig. 4 are in solutions with high concentration and the light blue spectra show the results obtained from solutions at lower concentration. No apparent concentration related spectral shifts are observed in the measured FTIR spectra, suggesting small and negligible effects of the concentration of the solutions on the IR spectra of Fc.

Fig. 5 compares the simulated IR spectra of eclipsed Fc in dioxane solution using three different models including polarizable continuum model (PCM) (Cossi and Barone, 1998), C-PCM (conductor PCM) (Cossi et al., 2003; Barone and Cossi, 1998) and SMD (solute molecule density) (Marenich et al., 2009), with the present FTIR spectral measurement in high concentration. The solute molecule density (SMD) model seems to achieve a slightly more accurate agreement with the measurement over the PCM and C-PCM models. The PCM and C-PCM solvent models only implicitly consider the solvation effects in the form of a polarizable continuum model rather than individual molecules. For example, the conventional PCM model (also called dielectric PCM or D-PCM (Tomasi et al., 2005)) treats the solvent as a polarizable dielectric continuum medium. For non-polar solvents the PCM and C-PCM models do not show significant differences of the calculated IR spectra of Fc. The solute molecule density (SMD) model is a continuum solvation model based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent.

Fig. 6 compares the simulated IR spectra of the D_{5h} Fc in the region of 400–600 cm⁻¹ with the FTIR measurement in several solvents. The theory (simulation) used the DFT based B3LYP/m6-31G(d) model in conjunction with the SMD continuum solvent model to simulate the IR

Table 3

Comparison of the measured and simulated Fc IR spectral peak positions in solvents in the region of 400–1200 cm⁻¹.

-												
	ACN ($\varepsilon = 35.69$)			$DCM(\varepsilon = 8.93)$			$\text{THF}(\varepsilon = 7.43)$			$DOX(\varepsilon = 2.21)$		
	Expt.	Calc. ^a	Δv^{b}	Expt.	Calc. ^a	Δv^{b}	Expt.	Calc. ^a	Δv^{b}	Expt.	Calc. ^a	$\Delta \upsilon^{\rm b}$
v_1	480	467	-13	478	466	-12	479	467	-12	479	471	-8
v_2	496	484	$^{-12}$	495	484	$^{-11}$	495	485	$^{-10}$	495	489	-6
v_3	823	852	29	820	850	30	820	851	31	821	845	24
v_4	1006	1027	21	1005	1029	24	1005	1029	24	1006	1033	27
υ_5	1107	1133	26	1107	1134	27	1108	1134	26	-	1141	-

^a Simulation DFT model: SMD-B3LYP/m6-31G(d).

 b Spectral shift: $\Delta\upsilon=\upsilon_{calc.}\text{-}\upsilon_{expt}\text{.}$



Fig. 5. The simulated IR spectra of eclipsed Fc in the DOX solution using three different models (PCM, CPCM and SMD) with the FTIR spectral measurement in high concentration. The SMD model show slightly more accurate spectrum.

spectra of the D_{5h} Fc in THF, DCM, ACN and DOX solvents. The theoretical spectra of the D_{5h} Fc are produced in the present study *without any scaling* but the simulated spectra in Fig. 6 are presented with a blue shift ($\Delta\nu$) of 6 cm⁻¹ and 10 cm⁻¹ for DOX (ε = 2.25) and THF (ε = 7.52) solvents, respectively, and 11 cm⁻¹ for DCM (ε = 8.93) and ACN (ε = 36.64) solvents, respectively. The frequency shift ($\Delta\nu\sim\varepsilon$) relates to the solvent dielectric constant ε — when the solvent dielectric constant is smaller than ε = 8.93 (DCM), it slightly increases with the dielectric constant, but the increase hits a plateau at approximately ε = 8.93. As seen in Fig. 6, after small shifts, the simulated spectra based on D_{5h} Fc are consistent with that conformer being lowest in energy in all solvents and that the energy difference between the D5h and D5d forms is at least 10 kJ mol⁻¹.



Fig. 6. Comparison of the simulated IR spectra of the eclipsed Fc in the region of 400–600 cm⁻¹ with the FTIR measurement in various solvents. Small shift to align the larger peak is applied.

4. Conclusions

The present study reveals the dominance of the D_{5h} ferrocene conformer in solutions at room temperature. It combines Fourier transform infrared (FTIR) spectral measurements with theoretical simulation for the IR spectra of ferrocene in solvents, such as ACN, DCM, THF and DOX, respectively, in a region of 400–500 cm^{-1} . The measurements consistently agree well with previously available Fc IR spectra in CCl₄ solution of Lippincott and Nelson (1958) as well as the most recent IR spectral measurement in dichloromethane (DCM) solution (Duhović and Diaconescu, 2013). Furthermore, the Fc solutions in high and low concentrations in the measurements do not exhibit significant changes in the spectra in the region of $400-500 \text{ cm}^{-1}$, indicating that the effect of solution concentration is insignificant. The IR spectra of ferrocene are also simulated using density functional theory (DFT) based B3LYP/m6-31G(d) model in acetonitrile solution for both eclipsed and staggered Fc conformers. Both the calculated relative energies of the D_{5h} and D_{5d} forms and the IR band profile in the 400-500 cm⁻¹ region are consistent with the D_{5h} (eclipsed) conformer of Fc being lowest in energy in all solvents. While it is difficult to estimate the relative energies of the two conformers from these measurements the band profile suggests an energy difference similar to that obtained for solid solutions of Fc in paraffin (ca. 10 kJ mol⁻¹) (Trevorah et al., 2020). These observations support our previous assertion that the IR spectra can be combined with good quality DFT calculations to explore the geometry of Fc (Mohammadi et al., 2012).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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