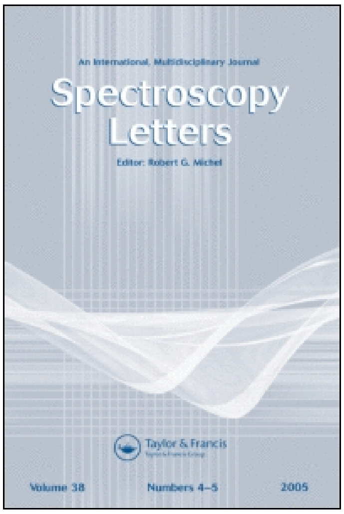

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The Vibrational Infrared Spectra of 1-Methyl-3-methylimidazolium Dimethylphosphate. Is the Dispersion-Corrected Functional Important in Intermolecular DFT Calculation of Ionic Liquids?

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The Vibrational Infrared Spectra of 1-Methyl-3-methylimidazolium Dimethylphosphate. Is the Dispersion-Corrected Functional Important in Intermolecular DFT Calculation of Ionic Liquids?

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ABSTRACT The vibrational infrared spectra of 1-methyl-3-methylimidazolium dimethylphosphate [MMIM][Me_2PO_4] have been studied using the *ab initio* density functional theory (DFT) method. The purpose of this study is to analyze and compare experimental and computed infrared spectra of the ionic liquid. Four DFT functionals with dispersion correction scheme, i.e., the dispersion-corrected B3LYP (B3LYP-D), PW91, PBE0, and M052X, were employed in order to have better prediction of some week bonds, which could be presented in the anion-cation interaction of the ionic liquid [MMIM][Me_2PO_4] complex.

KEYWORDS anion-cation pair, binding energy, density functional theory, dispersion correlation, infrared spectra, ionic liquids

1. INTRODUCTION

Molecular design, synthesis, and characterization of room temperature ionic liquids (ILs) have been the focus of many recent scientific investigations. ILs generated considerably excitement for environmental uses and many purposes as the consequence of the physical and chemical properties. They are usually non-volatile, non-flammable, thermally stable, and recyclable, thus making some chemical processes in the presence of ILs less expensive, more efficient, and environmental friendly.[1] One of the barriers preventing the adoption of ILs by industry was the dearth of physical property data for the compounds, as well as a general lack of fundamental understanding of the chemical constituents and structures of ILs.

Many efforts have been made to improve our understanding of the structure properties of the ionic liquids. In recent years, studies focusing on

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liquid and or gaseous-state characterization by theoretical calculations have appeared in the literature, whereby scientists were attempting to predict many of the physical properties of ionic liquids. For an example, scientists have employed quantum computational calculation to describe the carbon dioxide (CO_2) solubility in the ionic liquid solvents.[2] It was mentioned that the weak CO_2-ionic liquid interaction can be described by the presence of infrared frequency split in the CO_2 spectra. This particular case has allowed the opportunity to use the spectra analysis to find better absorbents for CO_2. However, few computational chemistry investigations were devoted to the infrared spectra, especially in an ionic liquid system. Talaty et al.[3] has initiated the study by analyzing the experimental infrared spectra data of $C_{2\text{-}4}$MIM imidazolium hexafluorophosphate and by comparing their findings with the calculated gaseous spectra of the same material by Hartree-Fock (HF) and density functional theory (DFT)-B3LYP method. They mentioned that DFT-B3LYP resulted in better prediction than HF method. Almost similar result was obtained by Heimer et al. by applying B3LYP calculation on imidazolium tetrafluoroborate ionic liquids.[4] Moreover, density functional theory is currently also preferable to be used due to its reasonable computational time for large group molecule calculation, such as cation-anion ILs. Unfortunately, some DFT functionals were not able to correctly handle/describe some chemical phenomena, such as the dispersion forces or van der Waals bond.[5] This is the problem that has to be solved. Currently, many proposed DFT functionals have been available in some commercial or non-commercial computational packet softwares. It can be mentioned here that most of them were successfully describe the presence molecular complexation, e.g., benzene dimmers by DFT-D.[6] Unfortunately, the literature reported the spectra analysis comparison between experimental and predicted values were still not available.

In the current study, we put an effort to study the infrared spectra analysis by some DFT-D functionals. 1-Methyl-3-methylimidazolium dimethylphosphate [MMIM][Me_2PO_4] was used as the object of the study. This investigation is a part of wide-range explorations to assess the value of computational chemistry in describing the physical-chemical phenomena. Inspired by the success of DFT-D functionals to describe dispersion interaction of some hydrocarbons and aliphatic system,[6] the study was focused on whether the dispersion correction can improve the DFT calculation for predicting the infrared spectra of ionic liquids system.

2. EXPERIMENTAL AND COMPUTATIONAL PROCEDURE

1-Methyl-3-methylimidazolium dimethylphosphate [MMIM][Me_2PO_4] was prepared using techniques described in the literature.[7,8] The vibrational infrared spectra of the ionic liquid were recorded experimentally with a Nicolet model 380 FTIR equipped ATR accessory at room temperature condition. The thermodynamic properties have been reported in the previous report.[9,10] In this study, the calculated infrared spectra were approached by modeling the ionic liquid in gaseous phase, following the previous investigation by Talaty et al.[3] The Gaussian03 program with e01 revision version[11] was used to perform the density functional theory (DFT) calculations. The main problem in DFT calculation of some molecular complexes was the weak-dispersion forces and physical absorption which could not be described correctly in some DFT functionals. Nowadays, the DFTs corrected by dispersion-correlation function have been used to address the presence of those kinds of interaction, such as stacking formation of molecule with π-system[12] or surface reaction over carbonaceous particle. Dispersion corrected-B3LYP (B3LYP-D) following the suggestion of Grimme[13] was becoming the most common functional to tackle the model where the van der Waals interaction is the dominant contribution for the potential energy surface (PES). The correction was done by adding the energy dispersion term to the normal DFT energy.

$$E_{total} = E_{DFT} + E_{disp}$$

while E_{disp} is an empirical dispersion correction given by

$$E_{disp} = -s_6 \sum_i \sum_j \left(\frac{C_6^{ij}}{R_{ij}^6} \right) \left(\frac{1}{(1 + \exp(-\alpha(R_{ij}/R_0 - 1)))} \right)$$

where R_0 is the sum of atomic van der Waals radii and α is a parameter determining the steepness of the damping function. The value of the atomic C_6 coefficients, and the R_0, α and s_6 parameters were obtained following the work of Grimme.[13]

This DFT functional has been tested and worked successfully to some complexes, such as B3LYP-D for benzene-dimer[6] and the binding energy of 156 non-covalent biological complexes taken from combined S22 and JSCH-2005 databases of Hobza et al. using BLYP-D.[14,15] Among previously known DFT functionals, PW91,[16] together with PBE0,[17] are among the rare functionals which include the dispersion correlation in its function at least in a qualitative way. A newly proposed DFT functional, M052X, created to have better prediction of thermochemistry and the problem of weak noncovalent interactions by Truhlar group was also employed.[18] In the benchmark calculations, the M052X functional was overpowered other functionals, such as BLYP, B3LYP, and PBE, in terms of PES calculation. And for the shake of comparison, a well known DFT functional, B3LYP, was also included in the test for comparison.

All geometries were calculated with a complete structural optimization without any constrains at 6-31G(d) and 6-311+G(2d,p) level of basis set. The first basis set was used to calculate relatively large complex which consists of two anions and two cations of [MMIM][Me_2PO_4] (see complex-3 of Fig. 1). However, the second basis set, which is larger than the first, was used to calculate single anion-cation pair of ionic liquid (see complex-1 and compex-2 in Fig. 1). As the normal procedure, before the analysis of frequency, the optimization was conducted in order to find any possible conformation of the complex. The vibrational analysis on all structures revealed a lack of imaginary frequencies, ensuring the presence of a true minimum. The total interaction energy (ΔE_{total}) was calculated as the difference between the complex energy and the monomers. The basis set superposition error (BSSE)[19] was corrected for all calculations using the counterpoise method. Similar to the interaction

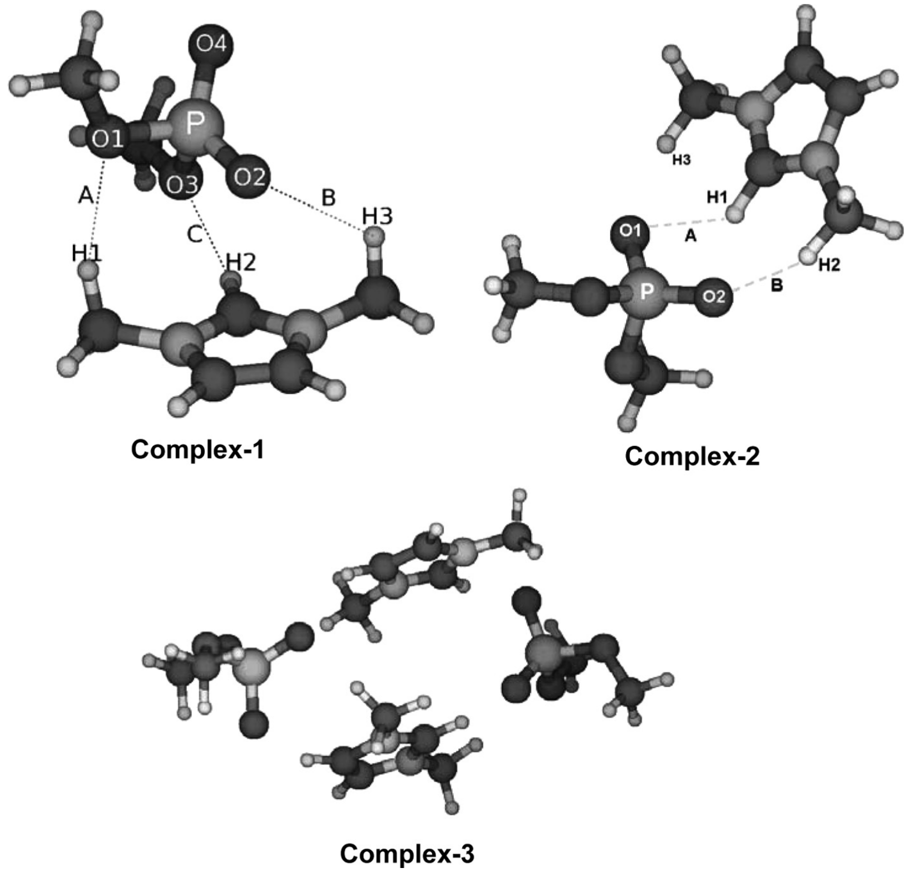

FIGURE 1 The optimized geometry of 1-methyl-3-methylimidazolium dimethylphosphate [MMIM][Me_2PO_4]. For complex 1 and 2, the optimized parameter values are shown in Tables 1 and 2.

energy calculation, the dispersion energy can be obtained from the difference value between $E_{disp.}$ of the complex and $E_{disp.}$ of the monomers.

In this current study, the calculated infrared spectra are presented without any scaling factor. In general, scaling factor is necessary to be done due to the problem of theory approximation, i.e., lack of electron correlation contribution, harmonic motion, and basis set deficiencies. However, by the absence of scaling factor (sf), we would like to explore the nature of the resulted vibrational spectra at sf = 1 by comparing those predicted spectra resulted by the DFT calculation.

TABLE 1 **The O–H Distances, Mulliken Charges, and Error Deviation (s) of the Optimized Conformation Complex-1**

Variable	B3LYP	B3LYP-D	PBE0	PW91	M052X
ΔE (kcal/mol)	−87,99	−95,6	−90,13	−90,57	−94,11
A (angs.)	2,4	2,3	2,4	2,2	2,3
B (angs.)	2,5	2,3	2,4	2,3	2,3
C (angs.)	2,1	2,3	2,1	2	2,3
qO1	−0,54	−0,56	−0,46	−0,44	−0,47
qO2	−0,7	−0,76	−0,66	−0,55	−0,75
qO3	−0,6	−0,6	−0,53	−0,48	−0,53
qH1	0,23	0,19	0,27	0,25	0,2
qH2	0,22	0,24	0,25	0,24	0,23
qH3	0,22	0,22	0,25	0,25	0,21
s (cm^{-1})	47,6	47,5	52,5	33,8	65,0

3. RESULTS AND DISCUSSION

3.1. Gas Phase Structures

3.1.1. Single Anion-Cation Pair

Inter-atomic or molecular interactions such as weak hydrogen bond, dispersion forces, and/or van der Waals are suspected to be present in many molecular complex-formed systems. The use of DFT with dispersion correction scheme functionals was believed able to reduce the quantity of the errors, despite this fact that DFT calculations are already quite successful in predicting accurate molecular structures and vibrational spectra. In this work, the vibrational spectra of [DMIM][Me_2PO_4] was treated as a gaseous complex, calculated by four different DFT functionals, in which are included the presence of dispersion of short-range correlation in qualitative and/or quantitative ways.

In general, all optimized DFT geometries gave almost similar structures one to the others. In mono anion-cation pair of [DMIM][Me_2PO_4], two complex conformations were found during the simulation. In both complexes, non-chemically bonding interaction between two or three oxygen atoms of dimethylphosphate [Me_2PO_4] with three hydrogen atoms of 1-methyl-3-methylimidazolium [MMIM] was clearly present. The global picture of anion-cation interaction of [MMIM][Me_2PO_4] is shown in Fig. 1 and the optimized parameter values of the structures are presented in Tables 1 and 2.

For the first conformation (complex-1), calculated by B3LYP, the nearest gap of the anion to the cation was 2.1 Å that separates the oxygen of the ester group anion [Me_2PO_4] from one hydrogen of methyl group of [MMIM]. As was predicted, the rich electron side of oxygen atoms of the cation will point out toward the lean electron side of [MMIM] to form a stable complex. This also occurs for two others oxygens which create weak-bonds with two hydrogens at the range between 2.4 and 2.5 Å. The inspection of HOMO configuration shows that the electron lobes in oxygen atoms are strongly present and pointing toward cation. The charge difference of between oxygen and hydrogen atoms creates an attraction force (electrostatic force) and reduces the repulsion between cation and anion. By *ab initio* calculation, Tsuzuki et al. found that at large negative charge (more negative) of oxygen could increase the contribution of the electrostatic energy to the interaction energy.[20] Calculated Mulliken charges of oxygens and hydrogens in the complex using B3LYP resulted values in the range of −0.7 to −0.5 for oxygen and 0.2 to 0.3 for hydrogen. For oxygen, these values are relatively highly negative, which can give contribution to the electrostatic energy around −80 to −70 kcal/mol.[21] Other DFT functionals

TABLE 2 **The O–H Distances, Mulliken Charges, and Error Deviation (s) of the Optimized Conformation Complex-2**

Variable	B3LYP	33LYP-D	PBEO	PW91	M052X
E (kcal/mol)	−94,76	−99,96	−97,21	−96,52	−99,11
A (angs.)	2,20	2,14	1,77	1,69	2,02
B (angs.)	2,24	2,20	2,04	2,00	2,12
qO1	−0,76	−0,78	−0,67	−0,59	−0,76
qO2	−0,83	−0,84	−0,81	−0,72	−0,90
qH1	0,22	0,25	0,30	0,30	0,24
qH2	0,21	0,24	0,30	0,28	0,26
s (cm^{-1})	57,23	47,98	30,81	32,73	67,63

resulted almost similar values of separation distance (Å) and Mulliken atom's charge. B3LYP-D, which was created based on normal B3LYP functional scheme, gave almost similar geometry with B3LYP where the O–H distance lies between 2.3 and 2.4 angstrom. PBE0 and PW91 were also found to be able to optimize the IL structure although these two functionals are not particularly meant for elaborating the presence of various weak-bond correlations. The separation distances of O–H calculated by PBE0 are in the range between 2.1 and 2.4 angstrom which are relatively similar to PW91 results (in the range of 2.0 to 2.3 angstrom). Compared with the previous two DFT functionals and with M052X, both PBE0 and PW91 gave a slightly different value of the atom's charges. For atomic oxygen, PBE0 and PW91 resulted average charge of −0.5, which is higher than B3LYP (−0.6), B3LYP-D (−0.6), and M052X (−0.56). Moreover, the charge for hydrogen was slightly higher ($qH = 0.25$) compared with B3LYP (0.22), B3LYP-D (0.23), and M052X (0.22). For the last functional test, we also included new DFT functional, M052X, obtained from the work of the Truhlar group.[13] The optimized geometry of [MMIM][Me_2PO_4] by this method resulted the structural structure close for the B3LYP-D as well as the atomic charges of oxygen and hydrogen.

The second complex (complex-2) was also distinguished by the presence of non-chemically bonding of two oxygens of the anion side with two or three hydrogens of the cation side (see Fig. 1 in complex-2). Compared to the first conformation, the potential energy of the second conformation is lower between ~6 and ~7 kcal/mol. This result is quite interesting, since the second conformer only includes the interaction of two oxygen atoms, i.e., O1 and O2, on the anion with three hydrogens (H1, H2, and H3). The electron lobes of two oxygens, O1 and O2 of HONO configuration confirm the idea that the anion is rich in electrons. Table 2 shows that the average charge of oxygen atoms that are facing cation has larger negative charges than complex-1. This will support the idea of Tzusuki et al.[20] that larger charges of oxygen can increase the electrostatic energy. As electrostatic energy is classified as attractive force, larger values mean it will contribute more to the total interaction energy. Since the average Mulliken charge of hydrogen atoms are similar, this situation will enable conformation complex-1 to have more attraction binding interaction and lower complexation energy than complex-2.

3.1.2. Double Anion-Cation Pairs

Instead of single pair cation [MMIM] and anion [Me_2PO_4], we included two cations and two anions to the model to investigate the effect on the predicted spectra. Because the size of the molecule is relatively large, the optimization and frequency calculation were done at lower basis set (6-31G(d)). Although a direct comparison between the previous two conformations of single anion-cation pair and the later case could not be done easily due to different basis set applications, a general picture of the trend is still possible to be drawn from the calculations done for a higher number of anion-cation system.

In the case of double anion-cation pairs, the interaction is still dominated by O of anion and H of cation. The HOMO analysis shows the similar picture of the previous two complexes where the electron lobes in all oxygen atom in anion side. In this case, we could expect that the [MMIM][Me_2PO_4] complex will have lower potential energy that previous two complexes. Calculate by DFT/6-31G(d), the complexation energies (ΔE_{total}) were laying between −250 and −220 kcal/mol (see Table 4).

3.2. Infrared Spectra

Figure 2 contains plots of experimental vs. theoretical vibrational frequencies from three complexes using the DFT/6-311+G(2d,p) for mono ion pair [MMIM][Me_2PO_4] and DFT/6-31G(d) for double pair [MMIM][Me_2PO_4]. The complete list of infrared vibrational frequency numbers and the assigned vibration are tabulated in Table 3. In general, the main distribution of the spectral can be divided into two major parts. The first part is in the range of 500 to 2000 cm^{-1} which dominated by phosphor and oxygen (P–O) vibrational modes of [Me_2PO_4] and carbon-hydrogen (C–H) of [MMIM] while the second is at 2700 to 3500 cm^{-1} which dominated by the carbon-hydrogen (C–H) vibrational modes of [MMIM]. The complete assigned vibrationals are listed in Table 3. The experimental data shows that the strongest region of the infrared spectrum is the combined P–O and C–O stretching at 1064 cm^{-1}.

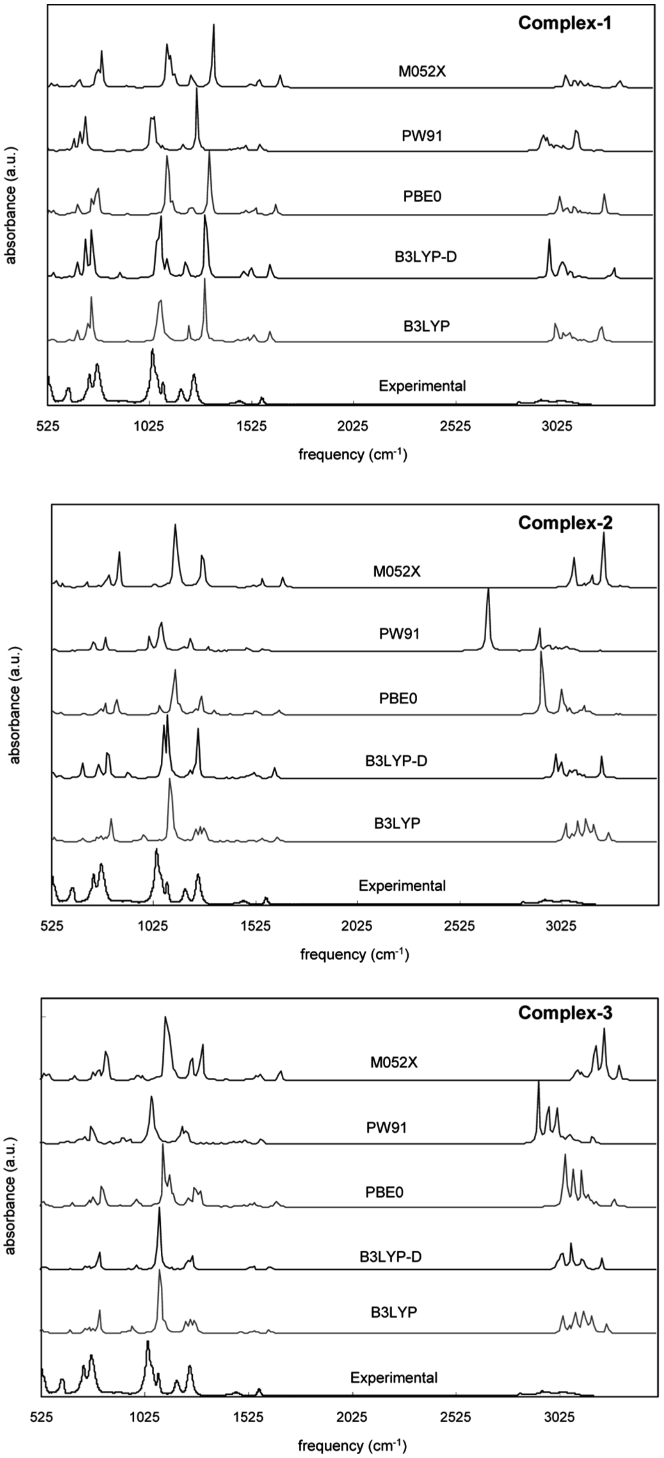

FIGURE 2 The experimental vs. predicted gas phase infrared spectra of [MMIM][Me_2PO_4]. *Note*. The scaled intensity was done by dividing each peak with the highest peak in each line.

The existence of this vibrational mode was confirmed by all DFT calculations although the position is slightly different one to the others. In normal treatment, this error could be reduced by manipulating the scaling factor the spectra or applying higher basis set to reduce the lack contribution of electrons correlation. Moreover, it could be mentioned here that all predicted spectra by DFT calculation satisfy the experimental result for [MMIM][Me_2PO_4] spectra in term of vibrational modes.

In order to clearly the difference shown in Fig. 2, we did an error analysis of deviation error, <s>, which is presented in the bottom line of Table 1 for complex-1 and bottom line of Table 2 for complex-2. The <s> value is calculated follows the equation of:

$$s = \sqrt{\frac{\sum_1^n (\bar{x} - x)^2}{n-1}}$$

As shown in Tables 1 and 2, there is no significant error difference to the assigned frequency number (υ) because of different structure of complex. Taking an example of B3LYP-D, the error deviation <s> of complex-1 was 47.5 cm^{-1} and only slightly changes to 48 cm^{-1} in complex-2 and 52.6 cm^{-1} with two pairs of cation-antion (complex-3). This is quite interesting point since: (1) different conformations or cation-anion's pair number will not change significantly to the assigned frequency (υ) numbers; (2) some dispersion-corrected DFT functionals did not improve the predicted spectra of the [MMIM][Me_2PO_4], taking an example that PBE0 and M052X produce higher <s> value than B3LYP for complex-1. For the first point, this error could be reduced by setting the scaling factor for each DFT functionals depend on the natural symmetric vibrations. Scaling procedure must be done due to imperfectness of the calculation method. Moreover, it is interesting to see that this is the second point at which DFT functionals seem not to be working well. In order to analyze this phenomenon; we conducted an energy calculation of the complexes to see the contribution of dispersion to the total interaction energy. Table 4 tabulates the total interaction and dispersion energy. Surprisingly, dispersion was contributing only a tiny fraction to the final interaction energy. Zhan et al. were able to show that electrostatic interaction plays a significant role in forming ionic pairs that turned out to be very stable with interaction energy over 90 kcal/mol.[22]

Although there is no significant different of the υ spectra number, different complex systems will give more influence on the intensity of the spectra. By carefully examine Fig. 2, the distribution of spectra

TABLE 3 Vibrational Infrared Assignments (cm^{-1}) of [MMIM][Me$_2$PO$_4$]. The υ Values are Taken from the Frequency Calculation of Optimized B3LYP Geometry

	υ cal.			Intensity		
No	Complex-1	Complex-2	Assignment	Complex-1	Complex-2	Exp.
1	15.0		Cat-An tors	<1		
2		18.6	Cat-An tors		<1	
3	27.0		Cat-An bend	4		
4		31.6	Cat-An bend, CH3(N1) twist		<1	
5	44.0		Cat-An bend	4		
6		50.1	Cat-An bend, CH3(O) bend		4	
7	60.0	58.3	Cat-An bend, CH3(O) scissors	4	4	
8	74.6		Cat-An bend, CH3(O) asym bend	5		
9	77.3		Cat-An bend, CH3(O) bend	9		
10		82.8	Cat-An tors, CH3(O) scissors		<1	
11		84.9	Cat-An tors, CH3(N2) twist		<1	
12		94.2	CH3(N) asym twist, CH3(O) sym bend		<1	
13		101.4	CH3(N) sym twist, CH3(O) asym bend		<1	
14		106.7	CH3(O) asym bend, CH3(N1) twist		<1	
15	110.0		Cat-An bend, CH3(O) twist	4		
16	118.9	117.7	CH3(O) sym twist	4	<1	
17		128.6	CH3(O) asym twist		<1	
18	141.1		Cat-An tors, CH3(O) twist	14		
19	149.7	147.8	Cat-An tors, CH3(N) twist, CH3(O) twist	36	7	
20	156.7		CH3(N) twist	9		
21	176.4		CH3(N) twist	<1		
22	204.0		CH3(N) sym twist, CH3(O) bend	7		
23		209.0	C-N-C scissors		4	
24	212.0		CH3(N1) twist, CH3(N2) twist, CH3(O) bend	9		
25		223.1	CH3(O) asym bend		<1	
26	243.8	244.9	CH3(O) asym bend	4	4	
27	269.1	278.6	CH3(N) asym bend	<1	<1	
28	295.3	284.5	CH3(N) scissors	<1	<1	
29	352.7	335.3	PO4C2H6 asym bend	<1	<1	
30	376.0		Po4C2H6 sym bend	5		
31		384.2	PO4C2H6 asym bend		4	
32	425.5	422.2	N2C5H6 asym bend	<1	<1	
33	480.8	461.4	PO4C2H6 sym bend str	4	<1	
34	498.6		P-O2-CH3 asym bend	14		
35		502.6	PO4C2H6 sym bend		14	
36	531.9	524.6	P-O1-CH3 asym bend	11	5	419
37	605.1	608.6	N2C5H6 sym str	7	<1	115
38	633.6	625.9	Ring N1-C-C-N2 asym bend	18	<1	251
39	649.0	647.3	Ring N1-C-N2 sym bend	65	7	63
40		698.2	PO4C2H6 sym str		<1	
41	717.9		Ring asym str	256		209
42	732.2	714.8	Ring CH sym str, O1-P-O2 sym str	72	7	482
43	734.6	719.6	Ring CH sym str, O1-P-O2 sym str	45	11	230
44		727.3	N2C5H6 asym str		43	
45	789.3		O1-P-O2 asym str	4		73
46	839.1	827.6	Ring CH asym str	<1	<1	73
47		891.4	CH in N1-CH-C2 str	<1	<1	
48	1019.8		C-N2-C str, C-H str	14		272
49	1032.1		Ring CN sym str, CH str	67		691

(*Continued*)

TABLE 3 Continued

	υ cal.			Intensity		
No	Complex-1	Complex-2	Assignment	Complex-1	Complex-2	Exp.
50		1034.7	Bond N-C sym str		14	
51	1043.4	1038.4	C-N1-C str	164	14	827
52	1060.8	1047.0	C-O-C asym str	231	25	492
53	1076.9	1064.1	O-P-O sym str, ring sym bend	103	103	209
54	1088.6	1086.4	CH3(O) asym str, ring sym bend	40	103	649
55	1102.4		Ring asym bend	25		126
56	1112.2	1103.7	Ring sym bend	18	18	63
57	1122.8	1112.5	Ring CH3-N-C sym str, CH3(N) sym scissors	11	11	21
58		1123.9	N1-C-N2 str, CH in N-C2H2-N sym str, CH3(N) sym bend	5		
59	1163.3	1152.0	CH3(N) asym bend	7	4	15
60	1170.3		Ring asym bend, CH3(O) asym bend, P-O asym str	7		199
61	1172.7	1160.2	Ring sym bend, CH3(O) asym bend, P-O asym str	9	4	220
62	1175.2	1175.1	CH3(O) asym bend	9	9	251
63		1175.6	CH in CH3(O1) str		9	
64	1177.0		Ring sym str, CH3(O) asym bend	11		262
65	1201.7	1198.2	P-O-C sym str, CH3(O) sym str	90	25	84
66	1201.8	1199.0	P-O-C asym str, CH3(O) asym bend	90	25	84
67		1200.9	Ring asym str, CH3(N) asym bend		25	
68	1280.0	1277.9	O3-P-O4 asym str, CH3(O) sym wagging	360	<1	52
69	1216.1		Ring asym str, O-P-O asym str	16		942
70	1310.5	1313.0	N2C5H6 asym bend	14	7	21
71	1347.2	1366.1	N2C5H6 sym str	4	<1	21
72	1386.1	1384.6	N2C5H6 asym str	4	<1	21
73	1423.8	1440.1	N2C5H6 sym str	4	<1	31
74	1461.4	1444.7	CH3(N) asym wagging	4	<1	73
75	1466.7	1463.8	CH3(O) asym wagging	5	4	73
76	1468.0	1466.0	CH3(O) sym wagging	11	4	73
77	1481.2	1470.4	CH3(N) sym wagging	14	4	42
78		1484.6	CH in CH3(N2) str, CH3(N1) wagging		4	
79	1489.8	1485.5	C-H on CH3(O1) scissors	22	4	31
80		1489.5	C-H in CH3(N1) ssym str		4	
81	1492.2	1491.2	C-H in CH3(O2) scissors	22	5	31
82	1504.2		C-H in CH3(N1) scissors	7		
83	1508.4	1510.8	C-H in CH3(O) sym scissors	22	14	21
84	1509.6	1512.2	C-H in CH3(O) sym scissors	29	9	21
85		1520.0	C-H in CH3(N) asym scissors	36	4	
86	1511.2	1523.5	Ring sym str, C-H in CH3(N) sym scissors	22	<1	21
87	1514.0		C-H in CH3(N2) scissors	29		
88	1515.5		C-H in CH3(N) asym scissors	29		
89	1592.1	1598.6	N2C5H6 asym str	34	7	31
90	1605.2	1602.3	N2C5H6 asym str	12	7	
91	2909.0	2910.0	C-H in N1-CH-N2 str		356	
92	3005.3		C-H in CH3(N2) sym str, C-H in CH3(O2) str	67		
93	3008.6	3008.9	C-H in CH3(N2) sym str, C-H in CH3(O2) str	104	14	63
94	3020.8	3017.2	C-H in CH3(O1) sym str	72	18	63
95	3046.5	3048.5	C-H in CH3(N1) sym str	34	14	63
96		3055.7	CH3(N2) sym str		11	
97	3068.2	3073.8	C-H in CH3(O2) asym str	36	14	
98	3085.0	3082.8	C-H in CH3(O1) asym str	36	11	
99	3100.6	3102.9	C-H in CH3(O2) asym str	22	39	42

(*Continued*)

TABLE 3 Continued

No	υ cal.		Assignment	Intensity		
	Complex-1	Complex-2		Complex-1	Complex-2	Exp.
100	3102.3		C-H in CH3(N2) asym str	22		42
101	3105.7	3106.6	C-H in CH3(O1) asym str	20	39	42
102	3124.2		C-H in CH3(N2) asym str	11		31
103	3125.8	3128.9	C-H in CH3(N1) asym str	11	9	31
104		3134.1	C-H in CH3(N2) asym str		9	
105	3135.0	3149.2	C-H in CH3(N1) asym str	11	4	31
106		3150.4	C-H in CH3(N2) sym str, C-H in CH3(O2) str		4	
107		3276.8	C-H in N1-CH-N2 str		<1	
108	3270.9	3276.9	C-H in N1-C2H2-N2 asym str	4	<1	21
109	3288.4	3294.6	C-H in N1-C2H2-N2 sym str	5	<1	21

magnification is clearly different. In complex-1, all predicted spectra gave the strongest spectrum for P-O stretching of [Me_2PO_4] and C-H wagging of [MMIM] (in the υ region between 1260 and 1300 cm^{-1}). However, the experimental infrared spectra produced the maximum spectrum for asymmetric C-P-O stretching of [Me_2PO_4], at $\upsilon = 1040$ cm^{-1}. This spectrum is only the second strongest signal in the case of complex-1.

A more complicated case was found in complex-2, where the predicted strongest spectra have significant differences depending to the functional used in the calculation. PBE0 and PW91 resulted the strongest spectrum for C-H wagging of metyl group of anion ($\upsilon = 2920$ cm^{-1} for PBE0 and $\upsilon = 2650$ cm^{-1} for PW91). On the other hand, B3LYP and B3LYP-D spectra are almost similar to the experimental spectra, but B3LYP-D is still overestimating the magnitude of P-O stretching of [Me_2PO_4] and C-H wagging of [MMIM], $\upsilon = 1220$ cm^{-1} (the highest magnitude of the conformation 1). The spectra signal for M052X is relatively similar to the experimental result at the first region ($\upsilon < 2000$ cm^{-1}) but overestimating the signal for C–H wagging of metyl group ($\upsilon = 3080$ cm^{-1}) and C–H stretching ($\upsilon = 3230$ cm^{-1}) of the anion. Again, we can point to the previous result that the DFT-D functionals could not give better prediction to the spectra.

TABLE 4 Calculated Interaction and Dispersion Energy

Energy[1]	B3LYP	B3LYP-D	PBE0	PW91	M052X
Complex-1					
ΔE_{total}[2]	−88,0	−95,6	−90,1	−90,6	−94,1
ΔE_{BSSE}[3]	−86,9	−79,0	−88,8	−89,3	−91,6
$\Delta E_{disp.}$[4]	−6,8	−6,7	−7,1	−6,7	−8,8
Complex-2					
ΔE_{total}[2]	−91,7	−100,0	−97,2	−96,5	−99,1
ΔE_{BSSE}[3]	−90,3	−72,1	−96,1	−95,4	−98,2
$\Delta E_{disp.}$[4]	−8,4	−4,2	−4,4	−4,2	−4,6
Complex-3					
ΔE_{total}[2]	−112,2	−123,9	−114,6	−116,2	−118,0
ΔE_{BSSE}[3]	−104,4	−115,0	−107,6	−107,4	−111,8
$\Delta E_{disp.}$[4]	−8,6	−9,8	−9,9	−9,8	−11,7

Note. [1] All energies are in kcal/mol. For complex-3, all energies are average energies (ΔE for 1 pair anion-cation).

[2] The total interaction energy.

[3] BSSE-corrected energy.

[4] Dispersion energy. Except for B3LYP-D functional, the calculation was done at single point optimized geometry of each functional and recalculated by B3LYP-D functional.

The combination of two anions and two cations, in general, gave better magnification of the signals compare to the previous two complexes (see Fig. 2). Over estimation of the signals was still found for PW91, PBE0, and M052X in the region over $\upsilon > 2500$ cm^{-1}, which dominated by C-H vibrations of the cation. However, these errors were relatively smaller than the previous two complexes of single anion-cation pair. From this brief study, it clearly mentions that the complexation structure will strongly affect the signal magnification of the spectra. As the relative errors of two cation-anion pairs were reduced significantly in term signal magnification, more and more anion-cation pairs are recommended to be included in the model simulation.

4. CONCLUSIONS

The computational vibrational infrared 1-methyl-3-methylimidazolium dimethylphosphate [MMIM] [Me_2PO_4] has been conducted by using five different density functional (DFT) functionals. In this study, single and double anion-cation pairs were used. In the case of single anion-cation system, two conformations of the complex were found for [MMIM][Me_2PO_4]. In general, all predicted infrared spectra by DFT calculation were close to the experimental ones. As the dispersion contribution to the total interaction energy is relatively small, the dispersion-corrected DFT functionals gave a tiny contribution for the spectra prediction. It also shows that different complex configuration was not change the assigned vibration number of the frequency (υ) but mostly affect the magnification of the signal. This error can be reduced by increasing the number of anion-cation pair.

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