

Investigating the effect of solvent polarity on the IR and NMR spectra of acetone

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By

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Certificate

This is to certify that this dissertation entitled ***Investigating the effect of solvent polarity on the IR and NMR spectra of acetone*** towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Rugwed Lokhande at Indian Institute of Science Education and Research, Pune under the supervision of Dr. Anirban Hazra. Associate Professor, Dept. of Chemistry and co-supervision of Dr. Sayan Bagchi, Principal Scientist, National Chemical Laboratory, Pune during the academic year 2019-20.



Student



Supervisor

Declaration

I hereby declare that the matter embodied in the report entitled ***Investigating the effect of solvent polarity on the IR and NMR spectra of acetone*** are the results of the work carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. Anirban Hazra and co-supervision of Dr. Sayan Bagchi and the same has not been submitted elsewhere for any other degree.



Student



Supervisor

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Abstract

Both IR and NMR spectra of molecules are one of the most accurately measured quantities. The sensitivity of these two spectroscopic observables to the environment is investigated in the present study. Our quantum chemical calculations have shown that bond polarization of the carbonyl bond happens due to the external electric field exerted by solvent on the solute. This picture is used to explain the sensitivity of these two spectroscopic observables.

Further, to explain the redshift in IR there are two popular models in literature. One is the Vibrational Stark Effect (VSE) and another is the bond polarization model. Our study shows that there can be contributions from both of these models to the IR redshifts of C=O stretch of acetone and further, the study shows that the contribution due to VSE is around one and a half times more than the bond polarization model.

Chapter 1

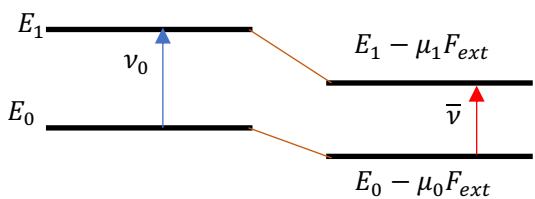
Introduction

It is well known that the IR and NMR spectra of molecules are sensitive to the polarity of the surrounding medium.¹ This sensitivity of these two spectroscopic observables with the surrounding medium (solvent) helps us understand the local electrostatics near the vicinity of the solute due to the external environment.² Hence, they play a significant role in modern chemistry as well as in biology. It is therefore important to obtain a fundamental understanding of this phenomenon.

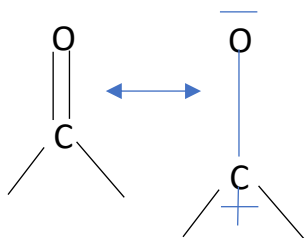
Carbonyls serve as an ideal candidate to understand the solvent effects on its IR and NMR spectra due to its highly local and intense IR nature and easy to obtain ^{13}C NMR spectra experimentally. The C=O IR stretching frequency of acetone ($\nu_{\text{C=O}}$) is redshifted in the polar solvent as compared to its frequency in the gas phase. This is also known as the vibrational solvatochromic shift.^{3,4} Further, this redshift was found to be increasing with increasing polarity of the solvent. Another independent spectroscopic technique ^{13}C NMR was carried out for the acetone, and this ^{13}C NMR chemical shift ($\delta_{\text{C=O}}^{13}$) for the carbonyl carbon increased with an increase in solvent polarity.⁵ Interestingly, ($\delta_{\text{C=O}}^{13}, \nu_{\text{C=O}}$) ordered pair when plotted showed a linear correlation with the regression value of $R^2=0.974$ (Fig 2).¹

In the present thesis, I have addressed three related questions: (I) Understanding the increase in redshift observed in the C=O stretching IR frequency ($\nu_{\text{C=O}}$) and downfield ^{13}C NMR chemical shift ($\delta_{\text{C=O}}^{13}$) values of the carbonyl moiety of acetone with increase in the solvent polarity. (II) Understanding the linear correlation of IR frequency and ^{13}C NMR chemical shift of carbonyl moiety of acetone. (III) Doing a comparative analysis of two different models widely used to explain the fundamental physical origin of IR redshifts of the carbonyl moieties. A brief description of these two models to explain the vibrational solvatochromic shift is given below.

A. Vibrational Stark Effect (VSE)



B. Bond Polarization



Sr. no.	Vibrational Stark Effect	Bond polarization
1	Shape of PES is constant	Shape of PES changes
2	Constant mechanical anharmonicity	Perturbed mechanical anharmonicity
3	Bond's force constant is fixed	Bond's force constant changes
4	Dipole difference is constant	Dipole difference may change

1

2

Fig.1 A cartoon representing VSE in an external Electric field (F) compared with the Bond Polarization picture. **2. Table 1** Comparison of various assumptions of VSE and bond polarization picture across different environment.

Vibrational Stark Effect

Vibrational Stark Effect can be explained in terms of the anharmonicity of the potential energy surface (PES) of vibrational normal modes. One immediate consequence of this anharmonicity of the PES is that the bond length in the first excited vibrational state is larger than the bond length in the ground vibrational state. If q is the effective charge associated with the bonded atoms which in VSE is assumed to be constant in the ground and the first excited vibrational state and also across the different environment, the dipole moment in the ground state will be $\vec{\mu}_0 = q\vec{d}$ and $\vec{\mu}_1 = q(\vec{d} + \Delta\vec{d})$ in the first excited vibrational state. Since these states have different dipole moments, they will get stabilized by solvent's external electric field (\vec{F}_{ext}) differently as explained in fig 1, hence, resulting in a redshift of the normal mode. The VSE assumes that $q, \vec{d}, \Delta\vec{d}$ is constant across different environment resulting in

$\Delta\vec{\mu}$ ($\vec{\mu}_1 - \vec{\mu}_0$), the dipole difference to be constant across environments.⁶ So, $\Delta\vec{\mu}$ is the intrinsic property of the oscillator independent of its environment. Hence, a linear relationship is obtained between redshift ($(E_1 - E_0) = \Delta\nu$) and \vec{F}_{ext} as $\Delta\nu = -\Delta\vec{\mu} \cdot \vec{F}_{ext}$.

Bond polarization picture

The electronic structure of the solute is affected by the electrostatic interaction between the solute and the solvent. This, in turn, alters the multidimensional potential energy surface (basically the anharmonicity of the PES) of the molecule and also the molecular structure as compared to in the gas phase. Varying the polarity of the solvent changes the anharmonicity of the PES accordingly. More distinctly, the change in the anharmonicity across different environments is accompanied by the altering of the partial atomic charges, equilibrium geometry of the molecule, bond's force constant leading to the change in the bond's strength of the bond as compared to those of isolated molecule. As a result, each vibrational mode undergoes a finite shift due to such solvatochromic effects.⁶ More distinctly, due to the polar environment polarization of the bond takes place making the bond weaker and hence causing the redshift.

1.1 Outline

The next part of the thesis will consist of the computational methodology used in this study. *Chapter 3* showcases and discusses the results obtained from the quantum chemical calculations. This chapter consists of three sections. (I) A simple bond polarization approach is discussed to explain the IR redshifts and the downfield ¹³C NMR chemical shift of the carbonyl moiety of acetone. (II) Discussions related to the understanding of the IR-NMR linear correlation of carbonyl moiety of acetone. (III) Comparative analysis of two different models used to explain the fundamental physical origin of the vibrational solvatochromic shift of C=O stretching normal mode of the carbonyl. *Chapter 4* concludes.

Chapter 2

Computational methodology

All the quantum chemical calculations were carried out for a single acetone molecule as a solute. Density functional theory (DFT) with B3LYP functional and 6-311g(d, p)++ cartesian basis set were used throughout all the calculations, including geometry optimizations, vibrational analyses (IR frequencies), ^{13}C NMR chemical shift calculations implemented in the Gaussian09 package. To include the solvent effect, Integral Evaluation Formulism of the Polarizable Continuum Model (PCM) was used by using the IEFPCM option in Gaussian09 package.^{7,8} Hessian calculations were done for the optimized geometry to ensure that optimized geometry (a stationary point) was indeed the true minima of multi-dimensional potential energy surface (PES) of acetone. Mulliken charges and dipole moments were also obtained by using the Gaussian09 package. In particular, Gauge invariant atomic orbitals (GIAO) theory was used for NMR calculations by using GIAO option implemented in Gaussian09.

For all the calculations where an electric field was used as a proxy to the solvent instead of using IEFPCM model, an uniform electric field was introduced along the dipole moment direction of the acetone molecule in the molecular Hamiltonian. The electric field option in Gaussian09 package was used for doing so. The geometry was optimized at every field value and all the calculations including vibrational analyses (IR frequencies), ^{13}C NMR chemical shift calculations, obtaining Mulliken charges on atoms and calculating the dipole moment were done for the optimized geometry.

Chapter 3

Results and discussions

3.1 Understanding the observed effect on IR and NMR spectra

The harmonic IR frequencies and ^{13}C NMR chemical shifts calculated using the IEFPCM model show a similar trend with varying the solvent as observed in the experiments. The C=O IR stretching frequency decreased with the increase in the dielectric constant of the solvent and ^{13}C NMR chemical shift ($\delta_{\text{C=O}}^{13}$) increased with the increase in dielectric constant of the solvent.

Table 2. Experimental C=O IR stretching frequency and ^{13}C NMR chemical shift of the carbonyl moiety of acetone as compared to the calculated C=O IR stretching frequency and ^{13}C NMR chemical shift using IEFPCM model.

Solvent ^a	Expt. $\nu_{\text{C=O}}$ (cm^{-1})	Calc. $\nu_{\text{C=O}}$ (cm^{-1})	$\Delta\nu_{\text{expt.-calc.}}$ (cm^{-1})	$\delta_{\text{C=O}}^{13} \text{ expt.}$ (ppm)	$\delta_{\text{C=O}}^{13} \text{ calc.}$ (ppm)	$\Delta\delta_{\text{C=O}}^{13} \text{ expt-calc.}$ (ppm)
Cyclohexane	1719.9	1768.47	-65.62	200.19	216.55	-15.56
DCM	1711.6	1746.67	-48.56	206.78	221.52	-14.27
THF	1716	1748.32	-35.06	204.19	221.20	-16.48
Chloroform	1710	1753.54	-32.31	207.10	220.13	-12.33
Acetonitrile	1712	1739.98	-43.53	206.56	222.76	-16.04
DMSO	1708	1739.40	-27.28	207.11	222.86	-15.62
Water	1697	1738.65	-41.55	215.37	222.99	-7.55

^aFrom top to bottom solvents are arranged in the order of increasing dielectric constant

There is a significant difference between the calculated and experimental IR and ^{13}C NMR values of the carbonyl, such that the calculated values are overestimated as compared to the experimental values (Table 2), though, the range of calculated IR frequency from cyclohexane to water (29.83 cm^{-1}) is comparable to range of experimental frequency (22.9 cm^{-1}) which implies that the calculated IR values are precise but less accurate. Similarly, the range of calculated ^{13}C NMR chemical shift values (6.44 ppm) deviates largely as compared to the experimental range (15.18 ppm) which implies that the calculated NMR values have low precision as well as low accuracy. When this calculated ($\delta_{\text{C}=\text{O}}^{13}, \nu_{\text{C}=\text{O}}$) ordered pair were plotted it showed an excellent linear correlation with a regression value of $R^2=0.99$.

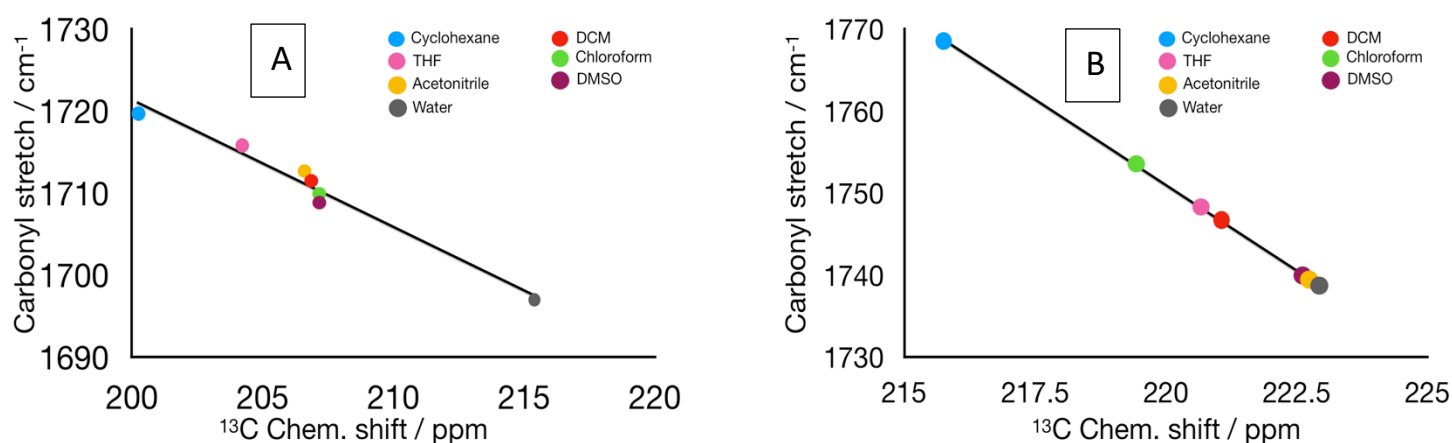


Fig 2. (A) Acetone carbonyl ($\text{C}=\text{O}$) stretching frequencies versus ^{13}C NMR chemical shifts of the carbonyl carbon dissolved in aprotic solvents of varying polarity and water. The black line represents the best fit line with $R^2 = 0.974$. (B) Calculated Acetone carbonyl ($\text{C}=\text{O}$) stretching frequencies versus calculated ^{13}C NMR chemical shifts of the carbonyl carbon by implementing IEFPCM model. The black line represents the best fit line with $R^2 = 0.99$.

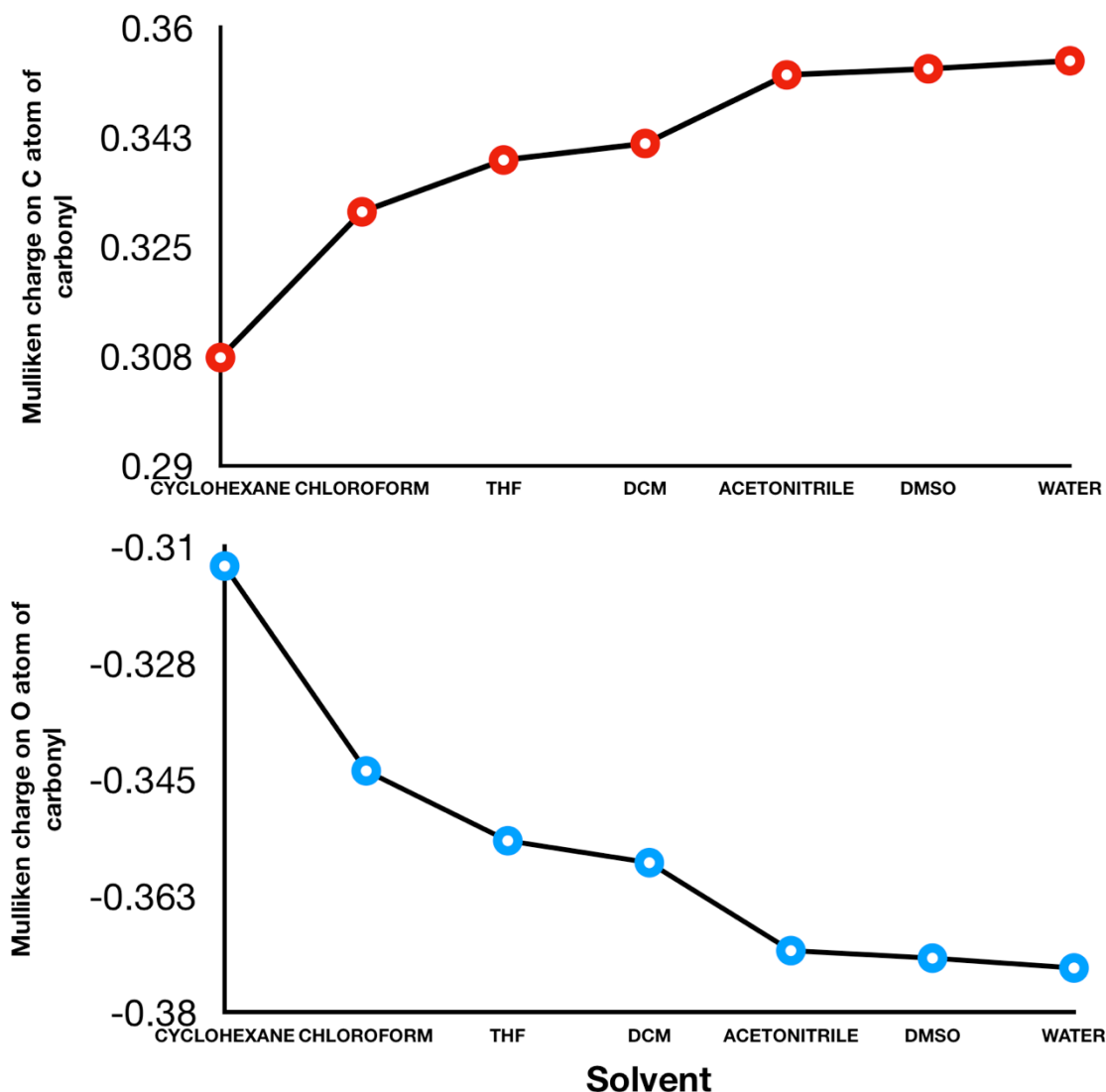


Fig 3. (A) Mulliken charge on the carbon atom of carbonyl vs. Solvent. (B) Mulliken charge on the oxygen atom of carbonyl vs. Solvent. IEFPCM model was used to implement the solvent effects. Solvents are arranged in increasing order of dielectric solvent in the direction of the x-axis.

In an attempt to understand the observed trend in C=O IR stretching frequency and ^{13}C NMR chemical shift with an increase in the solvent polarity, we calculated the Mulliken charges on carbon and oxygen atom of the carbonyl. Note that an increase in the dielectric constant of solvent is equivalent to an increase in the polarity of the

solvent. It was observed that as the solvents were arranged in increasing order of their dielectric constant along the axis and Mulliken charges on the y-axis, the magnitude of Mulliken charges on both carbon and oxygen atoms increased but in the opposite direction (Fig 3A and 3B). The electron density moves towards the oxygen atom as a function of increasing solvent dielectric constant. This charge separation implies that there is decreased electron density in between the carbonyl bond of acetone. This makes the carbonyl bond weaker. The weakening of the bond is accompanied by the decrease in force constant of the bond. Since the frequency is directly proportional to the force constant the increase in the magnitude dielectric constant of solvent increases the redshifts in the frequencies. In addition, the C=O bond length of acetone was also found to be slightly increasing with the increase in the solvent's dielectric constant.

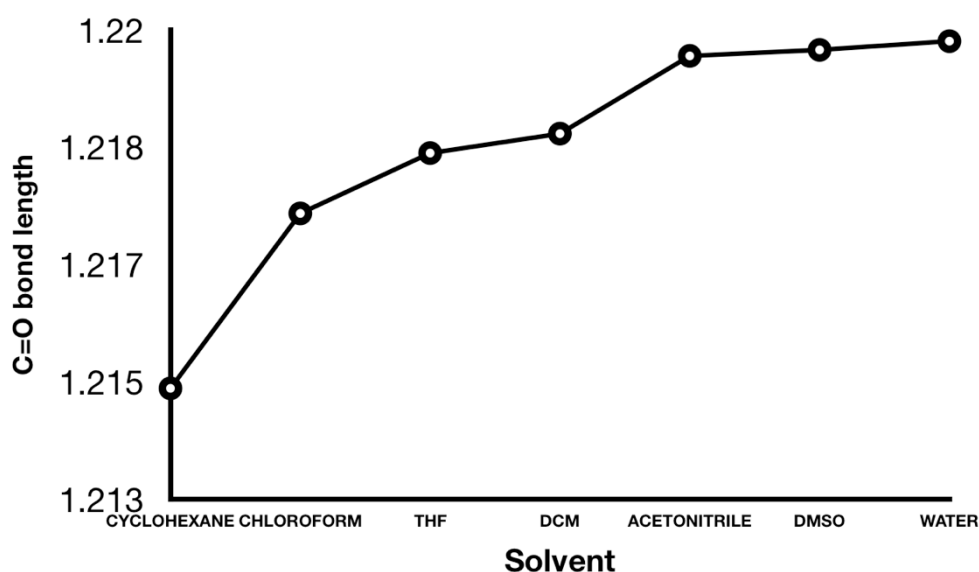


Fig 4. C=O bond length of acetone vs. solvent. IEFPCM model was used to implement the solvent effects. Solvents are arranged in increasing order of dielectric solvent in the direction of x-axis.

Similarly, the trend in ^{13}C NMR chemical shift can also be explained. The increase in the magnitude of the negative Mulliken charge on oxygen decreases the electron density on the ^{13}C carbon nucleus. It is also visible from the fact that the magnitude of positive Mulliken charge on the carbon nucleus is increasing (Fig 3B). One immediate consequence of this is the decreased electron density around the carbon nucleus. This leaves the ^{13}C carbon of carbonyl of acetone more deshielded to the external magnetic field applied during the NMR experiment. More deshielded nucleus gives a more downfield ^{13}C NMR chemical shift and hence the observed trend.

These quantum chemical calculations in a way supports the bond polarization picture where partial atomic charges are altered in the presence of a polar solvent. Also, a slight change in the C=O bond length was also observed as the magnitude of the field was increasing (Fig 4). This implies that the shape of PES is changing, thus changing the mechanical anharmonicity of the PES. These observations also go in the support of the bond polarization model for the redshifts.

3.2 Investigating the IR-NMR linear correlation observed in carbonyl compounds

It is very intuitive to think that the effect of the solvent on solute is to exert a net electric field on the carbonyl moiety which then affects its IR and NMR spectra. The field values exerted on the carbonyl moiety of acetone due to range of solvents can be calculated using MD by either using fixed charges or polarizable force fields.⁹⁻¹¹ A particular example of such calculated fields is shown in Table 3.

Table 3. The mean Electric field experienced by C=O bond of acetone in different solvents calculated by MD simulations. The values have been taken from reference 11.

Sr. no.	Solvent	Mean Field (MV/cm) ^a
1	n-Hexane	10.91
2	Tetrahydrofuran (THF)	30.63
3	Acetonitrile	36.11
4	Dimethyl sulfoxide	42.85
5	Water	69.5

^aThe direction of the field is along the dipole moment of the molecule. Standard deviations of these mean field values are also given in reference 11.

So, instead of using a PCM model, we incorporated electric field in the molecular Hamiltonian and redid the frequencies and chemical shifts calculations again. The reason for this is discussed later in this part. The direction of the field applied was along the dipole moment of the molecule. A schematic is also shown (Fig 5) that why does it make sense to apply a field in the direction anti-parallel to the bond axis i.e. parallel to the dipole moment of the molecule in case of acetone. Acetone being a

symmetric molecule, has its dipole moment oriented in the direction from atom O to atom C along the carbonyl bond.

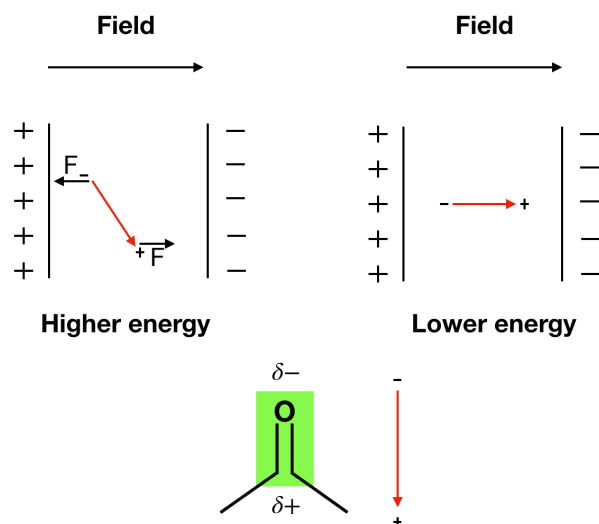


Fig 5. A schematic explaining how a dipole orients itself such that the direction of the dipole moment becomes parallel to the direction electric field applied.

A similar trend in IR and NMR values of carbonyl moiety of acetone was observed as in the IEFPCM model. As the magnitude of the field increases the C=O IR stretching frequency decreases and ¹³C NMR values increases.

From cyclohexane to water, the calculated field values range is around 10 MV/cm to 70 MV/cm as mentioned in table 3. In this range the frequencies take a range of around 1768-1738 cm⁻¹. Similarly, in the field calculations when the field is varied from around 10 MV/cm to 70 MV/cm the frequencies take a range of 1779-1736 cm⁻¹. Additionally, the range for ¹³C NMR chemical shift the range calculated using the IEFPCM model is 100-215 ppm and that calculated from the field model takes a range of 213-226 ppm. This range of frequencies and ¹³C NMR chemical shift calculated using IEFPCM model and the field model compares well.

These observations suggest that the solvent effect on the C=O IR stretching frequencies and ^{13}C NMR chemical shifts of the carbonyl moiety of acetone can be reduced to the notion that indeed it is the effective electric field exerted by the solvent on the C=O moiety of the acetone which causes the redshifts in IR frequencies and downfield shift in ^{13}C NMR chemical shift of carbonyl of acetone.

Fig 2A and 2B show a correlation between C=O stretching IR frequency and ^{13}C NMR chemical shift values of carbonyl moiety of acetone. In both figure a linear correlation between the two spectroscopic observables is visible. We wanted to investigate how long does the linearity of the IR-NMR correlation holds. We wanted to go in the field regime beyond the solvent's regime mentioned in Table 3. Since the solvents available in the PCM model covers only small regime of field (Table 3), an electric field model was chosen to proceed with calculations of IR and NMR values beyond the field regime of solvent and further this magnitude of the field can be increased as our per our requirement.

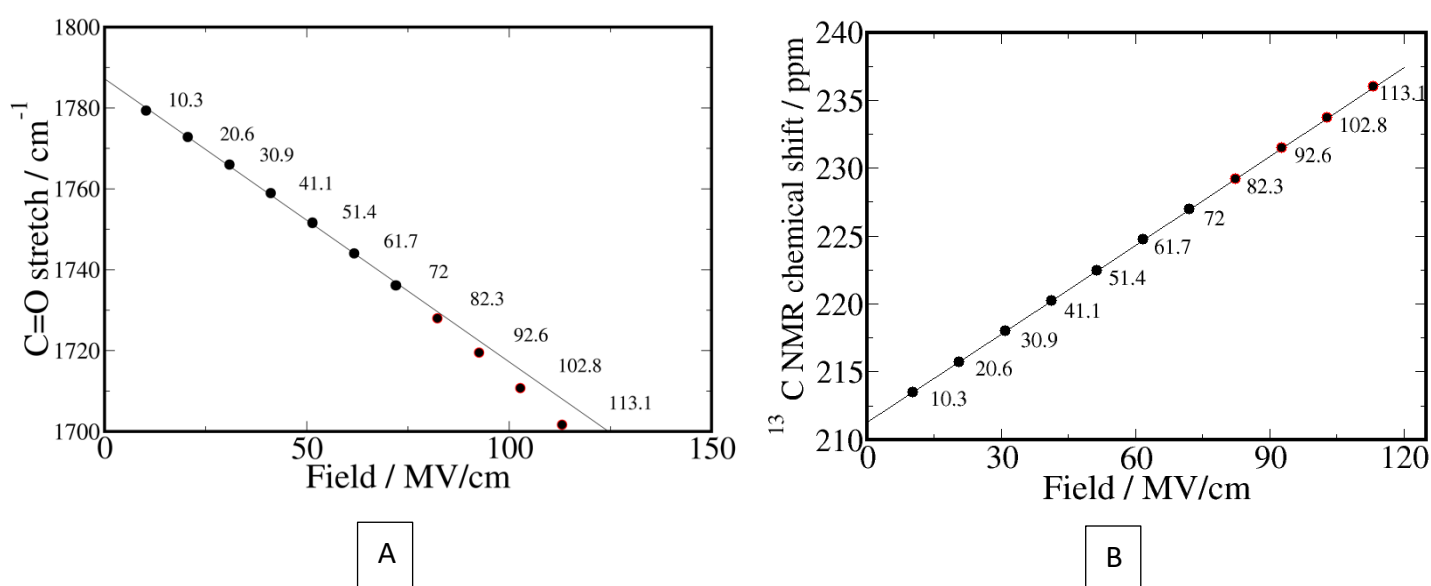


Fig 6 (A) C=O IR stretching frequency of acetone vs. the field. (B) ^{13}C NMR chemical shift of carbonyl moiety of acetone vs. the field. Field values in MV/cm corresponding to the coordinate are mentioned in the graphs. The linear line in both of the graphs are best fitted line for the first seven coordinates from the left i.e. the field regime of the solvent.

If C=O IR stretching frequency is linear with the field and ^{13}C NMR chemical shift of carbonyl carbon is linear with field then as a result the IR and NMR values of carbonyl moiety of acetone will also show a linear correlation as observed in fig 2. Now, this linearity will continue, until IR remains linear with the field consistently as well as NMR remains linear with the field consistently. If any of these spectroscopic observables breaks the linearity with the field this will also lead in breaking of the linear correlation of IR and NMR values of the carbonyl moiety of the acetone.

In fig 6A, the linear line in both of the graphs are best fitted line for the first seven coordinates from the left i.e. the field regime of the solvent. From the figure, it is clear that the linearity of C=O IR stretching frequency with the field breaks as we go to the field values beyond that of the field values exerted by common aprotic solvent on the carbonyl group. Though, the ^{13}C NMR chemical shift of the carbonyl carbon of the acetone still holds the linearity with field even in the extended regime. Since IR values are no longer linear with the field but ^{13}C NMR values are, this breaks the linearity of the IR-NMR correlation. So only in the small field regime this linear IR-NMR correlation holds. The linearity can be due to the fact that any of these two spectroscopic observables will be linear if the perturbation is smaller (here the perturbation is external electric field) if it is Taylor expanded in terms of the perturbation (field). As the magnitude of the field is increasing the higher order terms contributes a significant amount to values of these spectroscopic observables and these spectroscopic observables break the linearity with the perturbation (field). This in turn will also break the IR-NMR linear correlation observed in carbonyl compounds.

3.3 Comparative analysis between VSE and the Bond Polarization model

Now, under the harmonic approximation of the Potential energy surface (PES) corresponding to the C=O stretching normal mode of acetone one immediate consequence is that the bond length in the ground and the first excited state becomes constant. Since linear VSE assumes that the effective charge associated with the bonded atoms q is also constant in these two vibrational states, the dipole moment in these two vibrational states ($\vec{\mu}_0 = q\vec{d}$ and $\vec{\mu}_1 = q\vec{d}$) also remains constant and hence as a result of this $\Delta\vec{\mu} = 0$. This leads to equal stabilization of both of these states in presence of the external electric field (fig 7).

A. Vibrational Stark Effect (VSE)

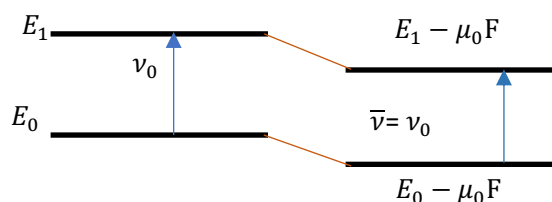


Fig 7. Since $\mu_0 = \mu_1$ in the harmonic approximation of the PES, there is equal stabilization of both of these states and no redshift takes place. Hence the calculated harmonic frequencies should show no redshift using the field model.

According to the assumption of VSE the shape of PES corresponding to C=O stretching normal mode does not change. And if it is the case, then in our quantum chemical calculations where the frequencies are calculated by approximating the PES as harmonic potential, it is expected that there should be no redshift. But indeed the

redshift was observed in the quantum chemical calculations of harmonic frequencies and this redshift increased with increase in the magnitude of the field. The plot of harmonic frequencies vs field is shown in fig 6A. So, indeed the shape of PES is changing. So, this leads to conclusion that, to the redshifts and also the rate of change of frequencies (redshift) observed w.r.t the environment (here field), there can be two different contributions, one arising from the harmonic frequencies calculations where the explanation of redshift goes hand in hand with the bond polarization picture also where PES is approximated as a harmonic potential and another contribution due to the VSE explanation as given in the introduction.

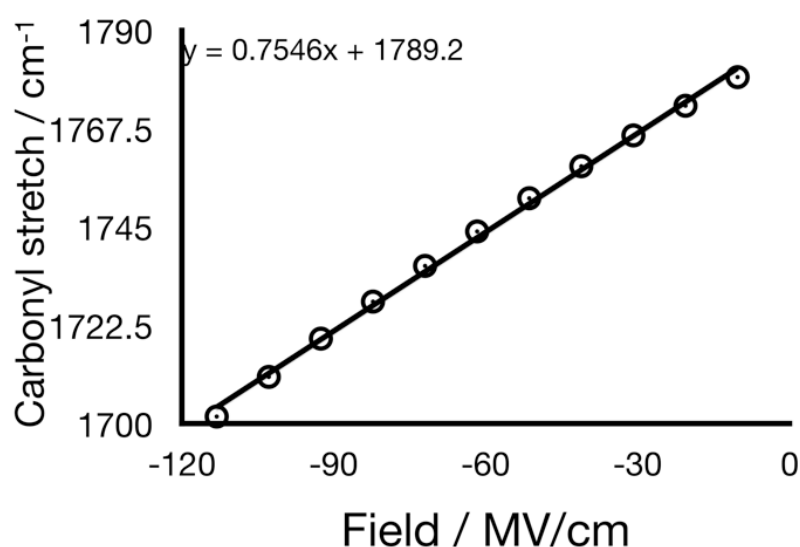


Fig 8. Calculated carbonyl IR stretching frequencies of acetone vs negative magnitude of field (right).

Now, the question is how does this two rates constants i.e the rate of change of the frequencies (redshift) observed w.r.t the environment (here field) compare. The rate at which the frequency is changing w.r.t field as calculated from quantum chemical calculations is nothing but the slope of graph in fig 8, which is $0.7546 \text{ (cm}^{-1}/ \text{MV/cm)} = 0.039 \text{ Debye}$. The rate at which the frequency should change w.r.t the field according

to VSE is the stark tuning rate i.e. the difference dipole ($\Delta\vec{\mu}$). Stark tuning rate was calculated by following the procedure explained below.

PES corresponding to C=O stretching normal mode was obtained by displacing the molecule along that particular normal mode and doing energy calculations. All this was done for the optimized geometry without any solvent effects or the field model. The molecule was displaced along the normal mode in the range -0.12 to 0.16 angstrom in the steps of 0.02 angstrom. The obtained PES was fitted to a Morse potential. The form of Morse potential is:

$$V^{Morse}(x) = a_0(1 - e^{a_1x})^2$$

The parameters a_0 and a_1 have been obtained by Non-linear least square fitting (NLLS) using xmgrace package. The analytical form of Eigenfunction of the Morse potential were already available.¹² This analytical form of the Eigenfunctions of Morse potential were used to calculate the expectation value of normal mode in the ground and the first excited vibrational state. Accordingly, the geometry of the acetone in the ground and first excited vibrational state was obtained. Using that geometry dipole moment calculations for both of these vibrational states were done using the Gaussian09 package. The difference of the dipole moment of the first state and the ground excited was calculated to be 0.067 Debye.

Chapter 4

Conclusions

1. (From the results and discussions in the section 3.1) In the presence of a polar solvent, polarization of the carbonyl bond of acetone happens and a simple bond polarization model can be used to explain the IR redshifts and downfield shifts of ^{13}C NMR chemical shift of the carbonyl moiety of acetone.
2. (From the results and discussions in the section 3.2) The IR-NMR linear correlation only holds in the smaller regime of the external field (the field regime of common aprotic solvents) applied along the dipole moment direction of the acetone molecules. This linear correlation of these two spectroscopic observables breaks in the extended regime of the field.
3. (From the results and discussions in the section 3.3) There is contribution from both the VSE and the bond polarization picture to the redshifts observed in carbonyl IR stretching frequency of acetone but VSE has around $(0.067 \text{ Debye} / 0.039 \text{ Debye} = 1.7)$ 1.7 times contribution than the bond polarization picture.

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